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Dynamics of phosphorus in soils and of nutrients in canopies of deciduous beech forests differing in tree species diversity

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Introduction

Sufficient supply of nutrients is a precondition for plant growth. In natural ecosystems this supply has to be furnished by mineralization in the soil or by deposition from the atmosphere. These processes are site specific and are modified by the plant community and its specific demand for nutrients (Eviner & Chapin, 2003; Hooper & Vitousek, 1998).
Phosphorus has been of interest in certain tropical forest ecosystems since a long time, because the productivity of these ecosystems is known to be often phosphorus limited (Vitousek, 1984). In temperate forests, research on phosphorus pools, concentrations and fluxes started together with the general research on forest nutrition and fertilization (Ulrich & Khanna, 1969), but was then neglected for several decades, because nitrogen was found to be the dominant growth-limiting factor in temperate forests. Due to industrialization, however, nitrogen deposition has increased tremendously, leading to nitrogen saturation of some forest ecosystems and to nutrient imbalances (Aber, 1992). Therefore, other macronutrients like phosphorus have or will become growth limiting. The present phosphorus status of forest trees is observed as suboptimal (BMELF, 1997; de Vries *et al.*, 2000). Hence, information about soil phosphorus pools, concentrations and transport as well as ecosystem phosphorus fluxes is needed to better understand forest nutrition at the present and future state and finally for forest management recommendations.

Large parts of Central Europe would be dominated by beech (*Fagus sylvatica* L.) forests if man had not intervened in forest development since hundreds of years (Ellenberg, 1996; Dierschke & Bohn, 2004). Large forest areas have disappeared due to conversion to urban and agricultural land. Existing forests are no longer natural, but man-made, managed, mostly even-aged, single species forest ecosystems. These forests are to a majority coniferous stands and beech forests play with 17% of the total forest area a minor role in Germany (DFWR, 2008). However, in the face of climate change, beech is assumed to have a high ecological and economic value since it is adapted to a large climatic range. In addition, it is recommended to establish mixed stands that are probably more adaptable to changes in the abiotic environment due to their higher diversity in several respects (genetic, functional, structural; Knoke *et al.*, 2008; Pretzsch, 2005). Hence, scientists recommend foresters to establish mixed species forests that are not even-aged, leading to higher species, functional and structural diversity (Baumgarten & von Teuffel, 2005; Fritz, 2006). In this context, beech and other deciduous tree species become more important in German forest management.

However, there are still a lot of open questions concerning tree species diversity and its effects on ecosystem functioning (Jones *et al.*, 2005). Results of studies that investigate the effects of tree species diversity on nutrient pools and cycling are ambiguous (Rothe & Binkley, 2001). Studies especially related to the link between phosphorus nutrition and tree species diversity are extremely rare. The present work will give answers to some of the open questions concerning the relationship between tree species diversity and soil nutrient pools as well as nutrient fluxes with litter turnover and deposition. Special emphasis is put on phosphorus and its general behavior in forest soils.

Biodiversity research in forests

At the present, there are several assumptions about how forest diversity may affect forest ecosystem functioning (Scherer-Lorenzen *et al.*, 2005). Ecosystem functioning includes ecosystem properties, goods and services (Christensen *et al.*, 1996). Here, only ecosystem properties are considered, which include sizes of compartments (e.g., pools of matter such as phosphorus or organic matter) as well as rates of processes (e.g., fluxes of matter among compartments). The way in which ecosystem properties may change due to shifts in forest diversity depends on several factors and more than 50 response patterns have been proposed (Loreau, 1998; Naeem, 2002). One possible response is the increase in ecosystem properties with increasing diversity. Two primary mechanisms explain this response (Loreau & Hector, 2001). (1) Species or functional richness could increase ecosystem properties through positive interactions among species (complementarity and facilitation) or (2) only one or a few species might have a large effect on a given ecosystem property (sampling effect). Complementarity results from reduced interspecific competition through niche partitioning. Facilitation takes place when one species alleviates the conditions of another species (e.g., provision of a critical resource). Complementarity and facilitation are the two primary mechanisms leading to the phenomenon of overyielding, in which production in mixtures exceeds expectations based on monoculture yields (Pretzsch, 2005). The sampling effect is given when the occurrence of a single species leads to an increase in an ecosystem property due to the species' functional traits and the increase is independent of the co-occurrence of other species (Hooper *et al.*, 2005).

The role of biodiversity in ecosystem functioning was in the beginning only studied in easily manageable, fast-growing systems like grasslands or microcosms (Scherer-Lorenzen *et al.*, 2005). These systems allow for experimental approaches and the diversity can be changed in order to study the effects on several functions of the systems. This kind of experimental

research is not easily assigned to forests since they are slow-growing ecosystems with long-lasting reactions to changes like addition or removal of species. In Germany, BIOTREE (BIOdiversity and ecosystem processes in experimental TREE stands) is an example of such a forest biodiversity experiment. Several deciduous and coniferous tree species were planted as monocultures and in mixtures with up to six tree species. However, results concerning tree species diversity in mature stands will only be available in several decades. To get around these long time spans until results are gained, the study of forest biodiversity does not only focus on experimental stands but includes also observational studies that compare existing (semi-) natural forest stands of differing tree species diversity. The advantage of observational studies is that old-growth forests are investigated, which have a natural trophic structure, tree age distribution and horizontal and vertical canopy structure (Leuschner *et al.*, 2009). Furthermore, the soil development is in a quasi-steady state. The German graduate school on forest biodiversity that frames the dissertation on hand is one example of such an observational study.

Framework of the dissertation

The present dissertation is a project of the DFG-graduate school 1086 “The role of biodiversity for biogeochemical cycles and biotic interactions in temperate deciduous forests”. This graduate school aims at investigating the relationship between biodiversity and forest ecosystem processes and their interactions in semi-natural, old-growth forests. In this observational study several disciplines work in close cooperation. Fourteen PhD projects are realized in the faculties of forestry, biology and agriculture and can be grouped together in the six main research areas of the graduate school:

(1) Biodiversity of organism groups other than tree species (mycorrhiza, understory vegetation, canopy and soil fauna);
(2) Biotic interactions;
(3) Biogeochemical cycles (C sequestration in biomass and soil, water turnover in trees and soil, nutrient turnover, mineralization, nutrient deposition and discharge);
(4) Modeling and geostatistics (water and nutrient turnover);
(5) Forest stand history;
(6) Economic evaluation.

The field work of the graduate school was done in the semi-natural, old-growth beech forests of the Hainich National Park in Thuringia (Central Germany; 51°06’N, 10°31’E). This National Park was founded in 1997 after being used for about 40 years as military training

area. Hence, the human impact has been low since many decades. In some areas of the Park pure beech forests are found, whereas in other areas beech occurs together with other valuable deciduous forest trees like lime (*Tilia cordata* Mill. and/or *T. platyphyllos* Scop.), ash (*Fraxinus excelsior* L.), maple (*Acer platanoides* L., *A. pseudoplatanus* L. and/or *A. campestre* L.) and hornbeam (*Carpinus betulus* L.). The tree species rich areas are probably due to selective cutting (Plenterwaldwirtschaft) and coppice-with-standards forestry (Mittelwaldwirtschaft), which foster species-rich stands (Schmidt *et al.*, 2009). The forest communities *Galio-Fagetum, Hordelymo-Fagetum* and *Stellario-Carpinetum* are found on soils with increasing clay content, pH, cation exchange capacity and base saturation (Mölder *et al*., 2006). The bedrock of the Hainich National Park is Triassic limestone covered with a loess layer of different depth. The soil type is a Luvisol (FAO, 1998). The soil texture of the loess layer is loamy to clayey silt and in the lower parts of the profile silty clay. During winter and spring the soil shows stagnic properties, during late summer it is mostly dry.

The differences in tree species diversity in an area that is otherwise relatively homogeneous (climate, bedrock) were ideal to select comparable forest stands of differing tree species diversity for an observational forest biodiversity study. In the north-eastern part of the National Park forest stands of different diversity level (DL) were selected:

(1) Diversity level 1: beech as the main tree species;

(2) Diversity level 2: beech, lime and ash as the main tree species;

(3) Diversity level 3: beech, lime, ash, maple and hornbeam as the main tree species.

For each diversity level four replicate stands existed. This kind of study is exceptional since four replicates of forest stands with up to five tree species but otherwise similar conditions are investigated in an old-growth, semi-natural forest ecosystem.

Scope of the dissertation

The biogeochemical cycles of the forest stands were investigated by several projects of the graduate school. The present dissertation especially focused on soil phosphorus and on the deposition and canopy exchange processes of nutrients.

Phosphorus plays an important role in the metabolism of all living organisms since it is part of ATP, DNA, RNA, phospholipids, certain sugars and other compounds. Phosphorus in soils is solely found as phosphate (PO_4^{3-}), which is protonated according to the soil pH. Especially in forest soils, a large proportion (about 50%; Attiwill & Adams, 1993) of the soil phosphate is organically bound (P_{org}). This organically bound phosphorus results from the incomplete mineralization of organic material originating either from plants (e.g., litterfall) or from the

turnover of microorganisms themselves. Plant roots are only able to take up phosphate ions which are not bound to other compounds. Organically bound phosphorus becomes plant available by complete mineralization to phosphate. In addition, mycorrhiza and also fine roots are able to split off the phosphate bound to organic matter or other compounds through exudation of phosphatases and organic acids, thereby providing additional phosphate for plant uptake (Attiwill & Adams, 1993). The recycling of organically bound phosphorus becomes increasingly important for the availability of phosphorus during pedogenesis (Walker & Syers, 1976). Hence, in the moderately weathered Luvisols of the investigated forests, inorganic phosphorus released from rocks plays a minor role in the phosphorus cycle. This fact points to the important role that trees may play in the cycling of phosphorus and thereby in their own phosphorus nutrition (Ulrich & Khanna, 1969). First, tree species differ in the demand for and the uptake of phosphorus, which leads to differing leaf phosphorus concentrations (Krauß & Heinsdorf, 2005) and may result in differing amounts of phosphorus entering the soil system annually with leaf litter. Second, different tree species contribute litter that differs in its decomposability (Gartner & Cardon, 2004), which may lead to different phosphorus turnover times. Third, the mycorrhiza community differs with tree species diversity (Lang, 2008), which together with different fine root systems results in differences in the exudates that influence the mineralization of organically bound phosphorus and the subsequent uptake of phosphate. Forth, tree leaves differ in their physical and chemical surface properties, which determine deposition of phosphorus and other airborne nutrients (André *et al.*, 2008) and the physiology of trees differs, influencing the canopy exchange rates of phosphorus and other nutrients (Tukey, 1970). Hence, different tree species compositions may lead to differences in the soil phosphorus pools, concentrations, turnover and input. These differences may either be due to a single key species or due to complementarity or facilitation effects of certain tree species mixtures.

The main part of the dissertation consists of three papers dealing with different aspects of soil phosphorus and nutrient cycling in the investigated forest stands:

(1) Soil phosphorus status and turnover in central-European beech forest ecosystems with differing tree species diversity;

(2) Phosphate sorption in the surface soil of a beech-dominated deciduous forest in Central Germany;

(3) Deposition and canopy exchange processes of beech forests differing in tree species diversity in Central Germany.

In the first paper, the soil pools and concentrations of inorganic and organically bound phosphorus are quantified. In addition, the annual turnover is estimated with data on the phosphorus content of leaf, herb layer and fine root litter from other projects of the graduate school. Differences between the diversity levels are evaluated considering the differences in the clay content of the soils. The second paper accounts for the lacking knowledge about phosphorus sorption and transport in forest soils compared with agricultural soils. The phosphorus sorption capacity is measured and the transport modeled for the investigated forest soils. This part of the phosphorus cycle is not dominated by tree species diversity but by the soil properties. The third paper deals with the deposition and canopy exchange processes of the investigated forest stands. Not only phosphorus but also other compounds were considered (Na^+, Cl^-, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, H^+, Mn^{2+}, Al^{3+}, Fe^{2+}, NH_4^+, NO_3^-, N_{org}). Canopy exchange processes are clearly dependent on the physiology of the trees and deposition processes are dependent on stand structural characteristics. Hence, the focus of the third paper again lies on the role of tree species diversity in nutrient cycling.

Hypotheses

One of the main hypotheses of the graduate school is that increasing tree species diversity enhances the exploitation of nutrients due to niche complementarity. Accordingly, the dissertation on hand hypothesizes that

(1) increasing tree species diversity increases the soil phosphorus pools and concentrations and accelerates the annual phosphorus turnover of the leaf, herb layer and fine root litter (Paper 1);

(2) phosphate sorption and transport in forest soils differs from that in agricultural soils and is dependent on soil properties (Paper 2);

(3) increasing tree species diversity increases the phosphorus and nutrient input to the soil due to changes in deposition and canopy exchange processes (Paper 3).

The validity of these hypotheses is evaluated in the discussion section of the dissertation. In more detail, these hypotheses are discussed in the three papers presented in the following chapters.

Declaration of the author's own contribution to the papers

The main part of the cumulative dissertation on hand is a series of papers. The first paper has been published in the European Journal of Soil Science, the second is ready for submission and the third is currently under review in a peer-reviewed journal. Ulrike Talkner is the author of all of the papers. She took the soil samples, did the laboratory work with additional help of the technical staff, analyzed the data, evaluated them statistically, produced all tables and figures and wrote the text. Furthermore, she is corresponding author for the journal editors and reviewers. The co-authors of the first and second paper are the supervisors of the dissertation and they contributed to the research idea of the papers. The additional co-authors of the third paper provided the samples of the rain water fractions and contributed to the manuscript of this paper.

Soil phosphorus status and turnover in central-European beech forest ecosystems with differing tree species diversity

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Phosphate sorption in the surface soil of a beech-dominated deciduous forest in Central Germany

U. TALKNER & F. O. BEESE

Abstract

Changes in phosphorus (P) nutrition of forests in Europe are expected due to nitrogen deposition and soil acidification. We studied sorption and desorption in soil samples of a deciduous mixed beech forest and tested the applicability of a P transport model. Due to the small-scale heterogeneity in soil properties, the samples differed in pH (4.1 to 7.0), clay content (12 to 42 %), effective cation exchange capacity (51 to 366 $mmol_c\ kg^{-1}$), soil organic carbon (15 to 57 $mg\ g^{-1}$) and total P content (215 to 663 $mg\ kg^{-1}$). These differences probably led to the observed differences in the amount of P sorbed by the soil samples. There was a tendency that the amount of P sorbed was increasing with decreasing pH. However, due to the collinearity of the soil properties, it was not possible to isolate the effects of single soil properties. All soil samples had in common that desorption of the previously sorbed P was incomplete (9 % on average). The P transport model that we used builds on the convection-dispersion equation and assumes adsorption to be the only storage process for P. It did not satisfactorily describe our data. Probably, processes other than fast adsorption have to be considered.

Introduction

The phosphorus (P) nutrition of many European forest ecosystems is or will possibly become impaired due to increased N deposition and soil acidification (BMELF 1997; de Vries et al. 2000). The former may lead to increased tree growth resulting in P fixation in the biomass and nutrient imbalances like increased N/P ratios (Flückiger and Braun 1998; Gradowski and Thomas 2008); the latter leads to increased P immobilization in the soil and therewith probably to reduced plant-availability of P (Carreira et al. 2000; Paré and Bernier 1989). This P immobilization is mainly governed by two processes, which are a fast reversible sorption of P onto soil surfaces and a slow almost irreversible process consisting of diffusion through the sorbing layer followed by precipitation or deposition (McGechan and Lewis 2002). The fast process involves a surface reaction and therefore can be described as adsorption, but the slow process that follows involves diffusive penetration into the adsorbing material (Barrow 2008).

Hence, Barrow (2008) used the word ‘sorption’ to describe both processes; all mechanisms by which surfaces may remove material from solution are included. In order to evaluate the current plant-availability of P and to estimate future changes due to further soil acidification, it is important to study these processes in unfertilized forest soils.

P sorption in soils has been studied to a large extent under natural and artificial conditions, mostly with respect to plant nutrition (e.g., Hinsinger 2001), P leaching to the groundwater (e.g., Goyne et al. 2008; Young and Briggs 2008) or P contamination of surface waters (e.g., Karageorgiou et al. 2007; Sharpley et al. 1994). Relationships between soil and sorption properties have been proposed. For instance, pH and clay content were related to P sorption parameters (Ige et al. 2007; Leader et al. 2008; Schwertmann and Knittel 1973). However, the results are ambiguous, because both positive and negative relationships were found.

Forest soils differ in several respects from other soils, especially agricultural ones. The P concentration of the forest soil solution is very low and leaching of P does seldom occur. The P cycle of forests is more closed than that of agricultural systems since the P taken up by trees mostly is returned to the soil via leaf and root litter. Therefore, forest soils contain more organic matter and are less homogeneous than agricultural soils. Forest soils are often more acid than agricultural soils, which leads to immobilization of soluble P by Al and Fe (hydr)oxides, which have a low solubility (Iuliano et al. 2007; Iuliano et al. 2008). Beauchemin et al. (1996) have reported that P sorption capacities were 50 % lower in agricultural than in forest soils and that the potential amounts of desorbable P in agricultural soils were two-fold greater than those of forested soils. Hence, it is of interest to study P sorption in unfertilized forest soils to gain insights into the relationships between soil properties and P sorption behavior of these soils.

We studied P sorption in a beech-dominated forest with differing amounts of other broad-leaved deciduous tree species on a Luvisol developed from loess, which is underlain by Triassic limestone. The soil properties of this contiguous forest area show small-scale heterogeneities in pH, clay content, effective cation exchange capacity (CEC_e), soil organic carbon (SOC) and total P content. The soil samples under study represented the spectrum of soil properties found in this area.

The aim of this study is to find out whether the small-scale heterogeneity in soil properties influenced the sorption and transport behavior of P and to describe the P transport with a transport model based on sorption isotherms obtained in the laboratory.

Materials and Methods

Study site

Soil samples were taken in a mixed broad-leaved deciduous beech forest in the Hainich National Park in Central Germany (51°5'N, 10°30'E). The three-year mean annual precipitation of the meteorological station 'Weberstedt/Hainich' (51°10'N, 10°52'E; 270 m above sea level) is 652 mm (meteomedia GmbH). The mean annual temperature is 7.5 °C and the study sites have a mean altitude of 340 m above sea level and a mean slope of 3.1 °. The soil type is a Luvisol (FAO 1998) developed from loess that is underlain by Triassic limestone. The thickness of the loess cover varies between 50 and 120 cm. The soil texture of the loess layer is loamy to clayey silt and in the lower parts of the profile it is silty clay.

Nine mineral soil samples were taken in 0 to 10 cm soil depth in an area with a radius of 4 km. The soil samples were air dried and subsequently sieved to less than 2 mm. The pH, clay content, effective cation exchange capacity (CEC_e), soil organic carbon (SOC) and total phosphorus (P) concentration were determined (Guckland et al. 2009; Talkner et al. 2009; Table 1). Although the soil samples were taken in one contiguous forest stand they exhibited different properties. This illustrates the small-scale heterogeneity in soil properties of the study site.

Soil number	pH_{H2O}	Clay	CEC_e	SOC	P_t
		%	$mmol_c\ kg^{-1}$	$mg\ g^{-1}$	$mg\ kg^{-1}$
4	4,1	16	85	15	551
1	4,2	14	70	20	215
7	4,3	12	51	38	263
9	5,0	21	94	24	374
2	5,1	33	146	36	536
8	5,2	36	158	33	573
5	5,6	26	142	33	225
3	6,5	42	341	57	486
6	7,0	39	366	53	663

Table 1 Properties of the forest soil samples (0-10 cm). SOC: soil organic carbon; CEC_e: effective cation exchange capacity; P_t: total phosphorus (P). The soil samples are sorted by ascending pH.

Batch experiment

The soil samples (8 g) were placed in glasses with a diameter of about 10 cm and a lid. A solution with differing P concentrations (0, 1, 2, 3 mg P L^{-1}; P in the form of KH_2PO_4) was added in a soil to solution ratio of 1 to 10. As background electrolyte 20 mM $CaCl_2$ was used.

The solution was gently hand mixed and left to attain sorption equilibrium at room temperature. After one day 10 ml of the solution was taken and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Spectro, Kleve, Germany) to determine the P concentration of the solution. The amount of P sorbed by the solid phase (soil) was calculated with Eq. [1].

$$q = V * (c_b - c_a) / m \quad [1]$$

q: amount of P sorbed (mg kg^{-1})

V: solution volume before the solution sample was taken (L)

c_b: P concentration of the added solution (mg L^{-1})

c_a: equilibrium P concentration of the solution (mg L^{-1})

m: soil mass (kg)

The samples were allowed to stand for a total of eleven days. Again, a solution sample was taken, analyzed and the amount of P taken up by the soil after eleven days was calculated according to Eq. [1]. Subsequently, the rest of the solution was removed and 20 mM $CaCl_2$ solution that contained no P was added in a soil to solution ratio of 1 to 10. After three days 10 ml of the solution was taken and analyzed as described above. The amount of P desorbed from the solid phase (soil) was calculated according to equation [1].

Sorption data after one day of all soil samples were fitted to a linear equation (Eq. [2]) and additionally to the Freundlich equation (Eq. [3]; Freundlich 1907).

$$q = a * c_a + b \quad [2]$$

a: slope of the fitted line (L kg^{-1})

b: y-intercept (mg kg^{-1}); that is, the amount of P already present in the soil before the sorption experiment

$$q = K_f * c_a{}^n + b \quad [3]$$

K_f: Freundlich constant (L kg^{-1})

n: Freundlich exponent

b: amount of P already present in the soil before the sorption experiment (mg kg^{-1})

In addition, the total amount of P sorbed after one day was calculated as the percentage of P applied and the amount of P desorbed as the percentage of P stored after eleven days.

To be able to compare the sorption behavior among the soil samples, the difference in sorption between two equilibrium P concentrations in solution was calculated (as proposed by Barrow 2008): between 0.02 and 0.08 mg P L^{-1} and between 0.4 and 0.5 mg P L^{-1}. These differences were used as dependent variables in linear models with the soil properties listed in Table 1 as explaining variables.

Breakthrough curves

Syringes with a diameter of 2.3 cm and a length of 10 cm were filled with 20 g of soil sample 1 to 6. The soil columns were wetted with a 20 mM $CaCl_2$ solution and afterwards continuously percolated with a 20 mM $CaCl_2$ solution that contained 20 mg P L^{-1} (in the form of KH_2PO_4). The $CaCl_2$ solution simulates the electrolyte concentration of the soil solution and avoids the dispersion of clay and the clogging of the setup. With a peristaltic pump, the percolation rate was adjusted to about (2.1 ± 0.2) ml h^{-1}. The percolated solution was continuously collected and analyzed for P by ICP-AES. After four weeks, steady state conditions were not yet reached. Nevertheless, we stopped percolating the columns with P-containing solution. Subsequently, the columns were percolated with 20 mM $CaCl_2$ solution that contained no P in order to desorb the sorbed P. Again, the percolated solution was continuously collected and analyzed for P. The P sorbed and desorbed was calculated by the input-output balance. At the end of the experiment the soil samples were dried to determine the pore water volume of each column (V_0).

The P breakthrough data were used to estimate transport parameters of the solute in the soil with the computer program CXTFIT (Toride et al. 1999). Different solute transport models can be chosen in the program and we used the simplest one, which is based on the convection-dispersion equation for one-dimensional transport of reactive solutes, subject to sorption, in a homogeneous soil. The model describes solute adsorption by the solid phase with a linear isotherm (Eq. [2] with b=0; that is, no P previously sorbed to the soil). The dispersion coefficients (D) were determined from the potassium (K) breakthrough curves. These coefficients were used in our fitting procedure of the P breakthrough curves. Hence, only the retardation factors (R) were fitted. In addition, the slopes (parameter a) of the linear equations of the batch experiment were used to calculate retardation factors of the soils according to equation 4.

$$R = 1 + \frac{\rho_b a}{\theta} \qquad \text{Eq. [4]}$$

ρ_b: soil bulk density (g cm^{-3})

a: slope of the linear equation (batch experiment)

θ: volumetric water content (cm^3 cm^{-3})

These retardation factors were used in the transport model and the resulting curves were compared to those obtained when fitting R from the breakthrough data.

All statistical analyses and graphics were made with R version 2.9.1 (R Development Core Team, 2007).

Results

Soil properties

The soil samples reflect the small-scale heterogeneity in soil properties of the study site. The soil samples 1, 4, and 7 were most acid (Table 1) with pH-values in the Al buffer range, according to Ulrich (1981). The soil samples 2, 5, 8, and 9 were in the silicate and samples 3 and 6 in the carbonate buffer range. The soil properties were correlated with each other, except for the total P concentration (Table 2). The total P content ranged from 215 to 663 mg kg^{-1} (Table 1).

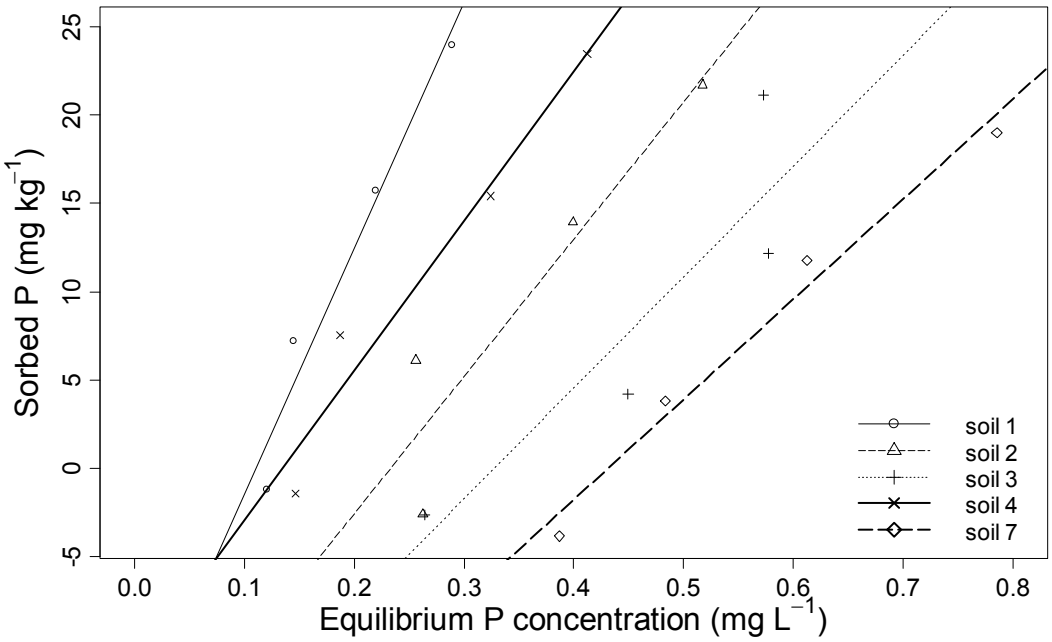
variable 1	variable 2	p	r
pH_{H2O}	Clay	0.002	0.87
pH_{H2O}	CEC_e	<0.001	0.95
pH_{H2O}	SOC	0.003	0.86
pH_{H2O}	P_t	0.20	0.47
Clay	CEC_e	0.002	0.87
Clay	SOC	0.02	0.75
Clay	P_t	0.05	0.66
CEC_e	SOC	0.004	0.85
CEC_e	P_t	0.09	0.60
SOC	P_t	0.36	0.34

Table 2 P-values and correlation coefficients of the Pearson's product-moment correlations with the soil properties as variables.

Batch experiment

The soil samples could be separated into two groups: the sorption behavior of sample 1, 2, 3, 4 and 7 was best described by a linear equation (Fig. 1a) and that of sample 5, 6, 8 and 9 by the Freundlich equation (Fig. 1b). To compare the sorption behavior among the soil samples of both groups, we calculated the difference in sorption between two equilibrium P concentrations in solution (as proposed by Barrow 2008): between 0.02 and 0.08 mg P L^{-1} and between 0.4 and 0.5 mg P L^{-1} (Table 3). The former range is the P concentration range found in the soil solution of the studied forest (unpublished data). There were no significant relationships between the difference in P sorption and the single soil properties presented in Table 1 (Table 4). In the higher concentration range (0.4 to 0.5 mg P L^{-1}), the pH explained 31 % of the variation in the amount of P sorbed. However, this negative relationship was not significant (p=0.12).

(a)



(b)

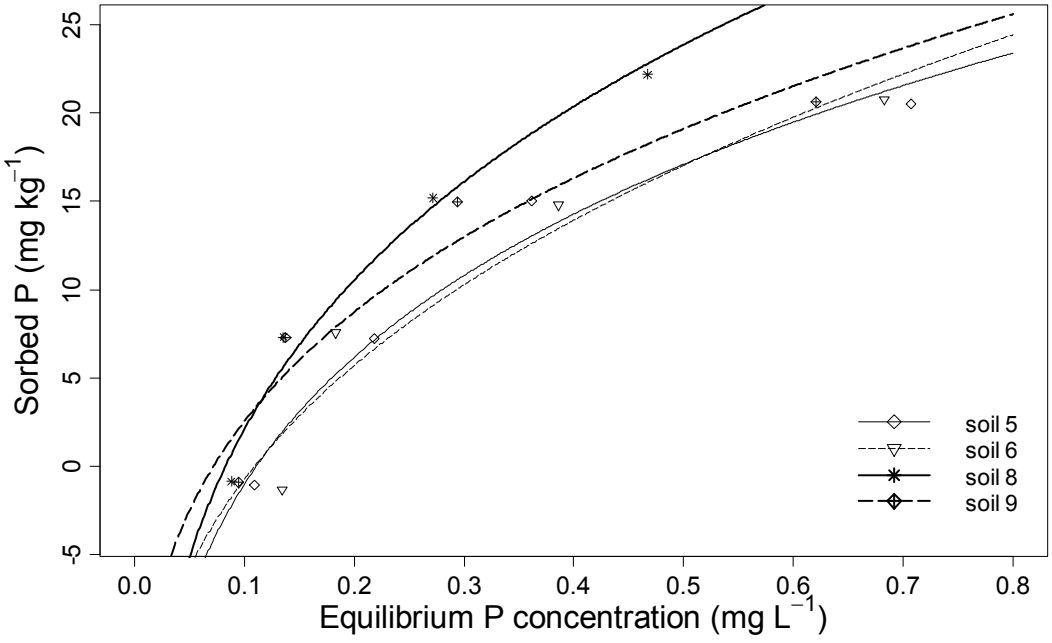


Fig. 1 Phosphorus (P) sorbed after one day of incubation with P-containing solution plotted against the equilibrium P concentration in solution; (a) soil samples 1, 2, 3, 4 and 7 are best fitted to a linear equation; (b) soil samples 5, 6, 8 and 9 are best fitted to the Freundlich equation.

Soil number	Model	a	b	n	R^2	P_{sorb} 1	P_{sorb} 2
		L kg^{-1}	mg kg^{-1}			mg kg^{-1}	
1	Linear	140	-15	-	0.97	8	14
2	Linear	78	-18	-	0.90	5	8
3	Linear	63	-21	-	0.86	4	6
4	Linear	85	-11	-	0.96	5	8
5	Freundlich	85	-58	0,17	0.98	12	3
6	Freundlich	52	-24	0,35	0.94	8	3
7	Linear	57	-25	-	0.98	3	6
8	Freundlich	85	-49	0,22	0.99	13	4
9	Freundlich	54	-25	0,29	0.94	9	3

Table 3 Model parameters of the batch experiment. Soil samples 1, 2, 3, 4 and 7 were best fitted to a linear equation (y=a*x+b), soil samples 5, 6, 8 and 9 to the Freundlich equation ($y=a*x^n+b$); the coefficient of determination (R^2) for each fit is given. P_{sorb} is the difference in sorption between two equilibrium P concentrations in solution; P_{sorb}1: P equilibrium concentration range of 0.02 to 0.08 mg L^{-1}; P_{sorb}2: P equilibrium concentration range of 0.4 to 0.5 mg L^{-1}.

P_{equ} range	——pH_{H2O}——			——Clay——			——CEC_e——			———SOC———			———P_t———		
Mg L^{-1}	relation	p	R^2	relation	p	R^2	relation	p	R^2	relation	p	R^2	relation	p	R^2
0.02 - 0.08	pos.	0.74	0.02	pos.	0.69	0.02	neg.	0.95	<0.01	neg.	0.58	0.05	neg.	0.88	<0.01
0.4 - 0.5	neg.	0.12	0.31	neg.	0.24	0.19	neg.	0.36	0.12	neg.	0.28	0.16	neg.	0.47	0.08

Table 4 Results of linear regressions with the batch experiment data. The soil properties were used in separate regression analyses to explain the variation in the amount of phosphorus (P) sorbed in two different equilibrium concentration ranges (P_{equ} range). CEC_e: effective cation exchange capacity; SOC: soil organic carbon; P_t: total P.

Most of the samples sorbed 59 to 80 % of the applied P after one day, only sample 3 and 7 sorbed less (42 and 38 %, respectively). After eleven days 63 to 85 % of the applied P was sorbed, with sample 3 and 7 still having the smallest amounts (44 and 56 %, respectively). There was a tendency that the samples whose sorption behavior was best described by a linear equation (sample 1, 2, 3, 4 and 7) showed increasing amounts of P sorbed relative to the amount of P applied to the soil. The soil samples desorbed between 0 and 44 % of the P sorbed after eleven days (on average: 9 %).

Percolation experiment

The properties of the soil columns that were used for the percolation experiment were similar (Table 5). Yet, the breakthrough curves exhibited different patterns for the different soil samples. They had in common that the samples all still sorbed phosphorus after the columns

had been percolated about 80 times (V/V_0=80) and the desorption part of the experiment was started (Fig. 2). The breakthrough curves of sample 2 and 5 showed a similar course (Fig. 2b and e); these two samples had very similar soil properties (Table 1), with pH value, clay content, CEC_e, and SOC in the mid range of all values. The desorption part of the most acid soil samples 1 and 4 was more retarded than that of the other samples (Fig. 2a and d). The soil samples 2, 3 and 5 sorbed most of the P until the columns were percolated approximately 5 times (V/V_0~5; Fig. 2b, c and e). This period was longer for sample 6 (V/V_0~10; Fig. 2f) and 1 (V/V_0~15; Fig. 2a). Sample 4 was most special in this respect and sorbed almost all of the P until the column was percolated approximately 40 to 50 times (Fig. 3d).

Soil	ρ_b	V_0	θ	l	v
	g cm^{-3}	cm^3	cm^3 cm^{-3}	cm	cm d^{-1}
1	1.11	10.47	0.58	4.34	21.37
2	0.96	13.29	0.64	5.02	21.71
3	0.89	14.88	0.66	5.41	18.80
4	1.27	8.23	0.52	3.80	23.47
5	0.96	13.32	0.64	5.03	20.25
6	0.93	14.02	0.65	5.20	16.25

Table 5 Properties of the soil columns used in the percolation experiment. ρ_b: bulk density, V_0: water volume, θ: water content, l: length of the soil column, v: average pore-water velocity.

The sorption part of the breakthrough curves was generally better described by the model than the desorption part. The model fit was worst for soil sample 4 and 6, which had the lowest and the highest pH, respectively (Fig. 2d and f). The beginning of the sorption part of soil samples 2, 3 and 5 was very well described by the model, but after V/V_0~20 the fit was becoming worse (Fig. 2b, c and e). The sorption part of sample 1 was fairly well described by the model (Fig. 2a). The desorption part of sample 1, 2, 3 and 5 was less retarded than fitted by the model (Fig. 2a, b, c and e).

The soils sorbed between 53 and 85 % of the applied P during the percolation experiment (Table 6). The most acid soil samples 1 and 4 sorbed least and most P, respectively. Only 4 to 19 % of the sorbed P was released during the desorption part of the percolation experiment. There was a clear distinction between the most acid soil samples 1 and 4, which desorbed relatively more P than the less acid soils.

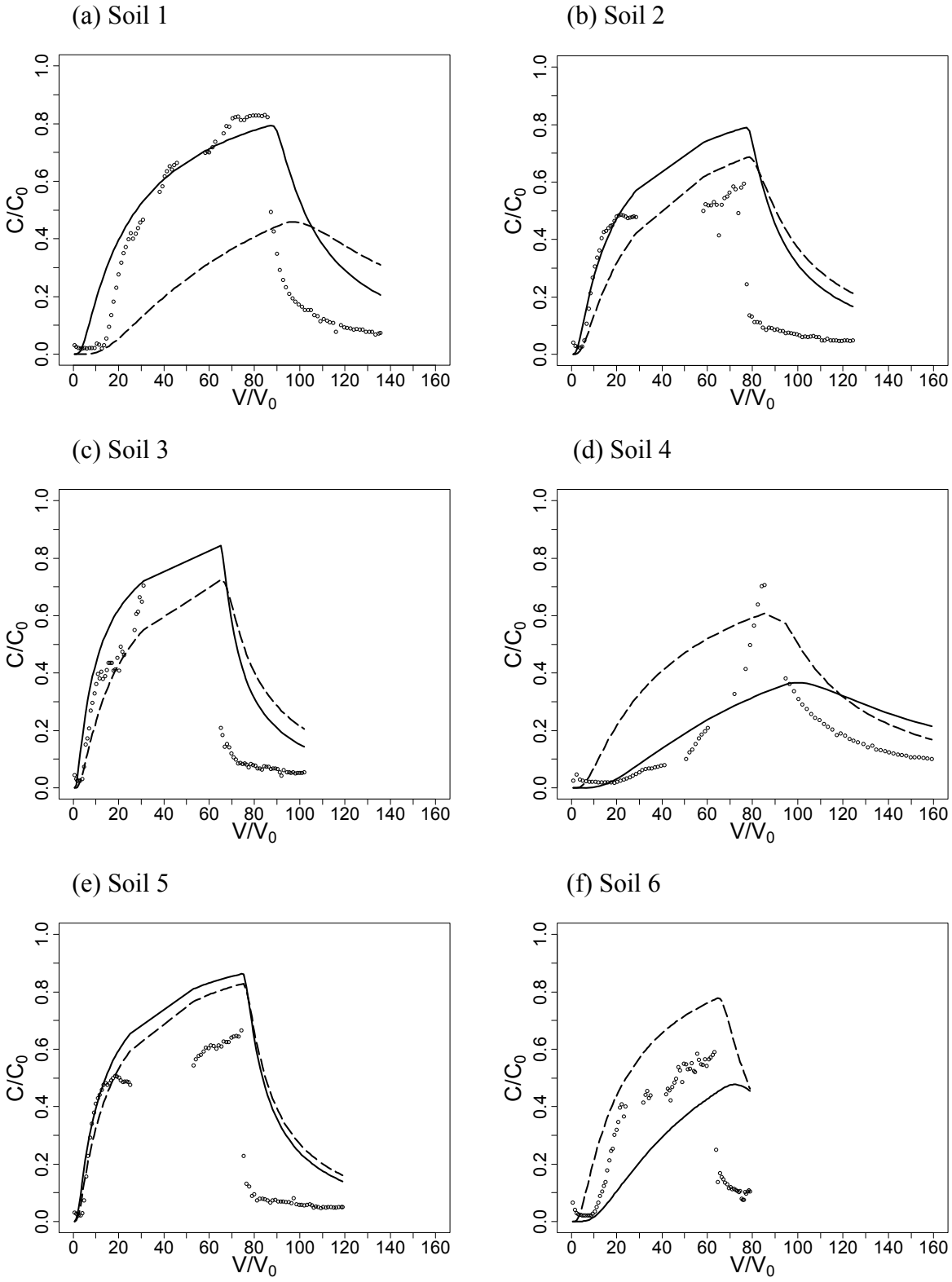


Fig. 2 Breakthrough curves for phosphorus (P). The dots are the measured values, the lines are the curves fitted with the parameters of the percolation experiment and the dashed lines are the curves fitted with the parameters of the batch experiment, both according to the convection-dispersion equation.

	P		
Soil number	applied	sorbed	desorbed
	mg kg^{-1}	%	
1	899	53	16
2	1012	62	7
3	954	66	7
4	702	85	19
5	987	57	7
6	887	68	4

Table 6 Amounts of phosphorus (P) applied (mg kg^{-1}), sorbed (%) and desorbed (%) during the percolation experiment.

The retardation factor R of the transport model is a measure of the interaction of the solute with the soil; R is one if there is no interaction at all and gets larger with increasing interaction (Table 7). Given the soil bulk density and the volumetric water content, R can be calculated from the slope of a linear sorption equation (see Eq. [8]). Even though the sorption behavior of the soil samples 5 and 6 was better described by the Freundlich equation, we fitted a linear equation to all of the samples that were used in the percolation experiment. These slopes of the batch experiment were used to calculate R (Table 7). For sample 5, the fitted and the calculated retardation factor and the resulting curves were similar (Fig. 2e). For sample 2 and 3, R calculated from the batch data was larger than R fitted from the percolation data, hence, adsorption was overestimated (Fig. 2b and c). This was even more pronounced for sample 1 (Fig. 2a). On the other hand, for sample 6, the retardation factor calculated from the batch data led up to a V/V_0 of 30 to a better description of the breakthrough data than R fitted from the percolation data (Fig. 2f). The measured breakthrough curves for sample 4 were neither described well by the retardation factor from the percolation nor from the batch data (Fig. 2d). Hence, R calculated from the batch data only led to good descriptions of the breakthrough curves for part of the soils.

	Retardation factor R	
Soil number	Percolation	Batch
1	69	268
2	69	118
3	42	86
4	579	208
5	41	52
6	165	53

Table 7 The retardation factor (R) fitted from the percolation experiment data ('Percolation') and calculated from the parameters of the batch experiment data ('Batch').

Discussion

The soil samples could be separated into two groups according to their P sorption behavior: for one group it was best described by a linear equation, for the other with the Freundlich equation. There was a tendency that the more acid soil samples with low clay contents were best fitted by the linear equation and the soil samples with higher pH values and larger clay contents by the Freundlich equation. Hence, the small-scale heterogeneity of soil properties in the study area seemed to influence the sorption behavior of the soil samples.

However, the soil properties did only explain a small amount of the variation in P sorbed by the soil samples. Of all soil properties, the pH explained the sorption behaviour of the forest surface soil best: the amount of P sorbed in a given concentration range was increasing with decreasing pH. Reducing the pH increases the protonation of oxide-surfaces, which promotes the adsorption of P (Darrah 1993). In contrast, the clay content seemed to play a minor role in explaining the differences between the studied forest soil samples. In principal, the increase in clay content could have led to an increase in sorbing surface area of the soil samples, which would have increased the sorption of P. However, the clay content was positively correlated with the pH of the soil samples. Hence, the positive effect of increased clay content on P sorption could have been overcompensated by the negative effect of the pH on P sorption, which was observed in the studied soil samples. This makes it difficult to predict the P sorption of such soils.

The soil samples sorbed large amounts of the added P already after one day. This can be seen as the fast sorption process and one can assume that it would be reversible (McGechan and Lewis 2002; Barrow 2008). After eleven days, only 0 to 18 % of the applied P was sorbed additionally compared to the sorption after one day (in two cases even desorption occurred). Hence, the fast sorption process accounted for more P being stored in the soils than the slow processes. However, the desorption of the previously sorbed P is incomplete: on average only 9 % of the P sorbed after eleven days could be desorbed. This decline in kinetic availability of sorbed P with time is probably due to the slow sorption, which includes processes like diffusion of P to deeper sorption sites, occlusion of adsorbed P, conversion from monodentate to bidentate inner-complexes and precipitation of P with Al and Fe hydroxides (McGechan and Lewis 2002; Barrow 2008; Sanyal and de Datta 1991). These processes are not fully reversible and may have led to the observed retention of P in the soil samples. This implies that an increase of P in the forest soil solution leads to fast adsorption of P, followed by slow processes that lead to a stronger binding of P to the soil than the fast adsorption process. Hence, the longer the contact time of P with the forest soil, the stronger is the binding and it

may be assumed that this leads to decreased plant availability of P (Barekzai 1984). In the study site, the P concentration of the soil solution was very low (0.002 – 0.008 mg P L^{-1}, unpublished data) and P was efficiently sorbed by the soil samples, but this P was hardly desorbable. Hence, the plants either have to take up P very fast from the soil solution before it is sorbed by the soil or they have to use mechanisms that assist desorption of P. These mechanisms can be root-induced chemical processes (e.g., the release of exsudates; Hinsinger 2001) or the symbiosis with mycorrhiza (Schachtman et al. 1998). Furthermore, this illustrates the closed P cycle of forests.

During the percolation experiment, the reaction time of P with the soil was more than one day. Hence, we cannot only speak about the fast sorption reaction, but the other slow processes that we named above probably also occurred. The course of the breakthrough curves depicts that the sorption of P was not continuous but proceeded in several steps for most of the investigated soil samples. This is typical when other processes than fast adsorption occur. In addition, the desorption of the previously sorbed P was incomplete and did not have the same course as the sorption part. In surface horizons of forest soils, the sorption front of breakthrough curves has been reported to appear later than in agricultural soils; this was attributed to a larger number of P sorption sites in the forest soils (Beauchemin et al. 1996). The desorption part of our breakthrough curves started with a fast P concentration drop in the percolating solution. This was also observed by Beauchemin et al. (1996) and interpreted as a great affinity for P and a resulting very weak desorption of previously added P. Most P was desorbed from the most acid soil samples 1 and 4, however, even those samples desorbed only 16 and 19 %, respectively, of the P sorbed. In these soil samples with low pH values instable P fractions must probably have formed, which did not form in the less acid soil samples. The expectation that relatively more P can be desorbed during the percolation experiment than in the batch experiment was falsified; even though the columns were percolated continuously with P-free solution.

The transport model that we used to describe the percolation did not completely satisfy the expectations; for some soil samples (e.g., sample 1) the fit was much better than for others (e.g., sample 4). Only adsorption is included as a storage process in the model and full reversibility of this process is assumed (Toride et al. 1999). The other processes that play an important role in the storage and transport of P are not included in the model; i.e., diffusion to deeper soil layers, precipitation/dissolution and complexation. Therefore, the desorption of P was highly overestimated by the model. The use of the retardation factor calculated from the parameters of the batch experiment led to an overestimation of the sorption part for soil

sample 1, 2, 3 and 5. Sample 4 was with both retardation factors badly described by the model since the breakthrough curve had an untypical course. For sample 6, the model fit with the retardation factor calculated from the parameters of the batch experiment led to an underestimation of the sorption part. Hence, the use of parameters of the batch experiment to describe P transport in these small columns only led to good descriptions of the breakthrough curves for part of the soils; for some soils at least the sorption part was fairly well described. The model performance would likely be improved with the inclusion of the slow P storage processes.

Conclusion

The sorption behavior of the investigated forest soil samples differed. However, the soil properties, which varied on a small scale in the study area, could only explain a small amount of the variation in the amount of P sorbed.

The forest soil samples sorbed large amounts of P after one day. However, this sorbed P was hardly desorbable when the contact time between soil and P containing solution was several days. Hence, this study emphasizes that at least the studied forest soil samples quickly sorbed P and that this P was transferred from the desorbable pool to a hardly desorbable pool within a short time. This pool is probably less plant-available than reversibly adsorbed P. Hence, increases of the soil solution P concentration seem to be of short duration and trees have to take up this additional P quickly before it is sorbed by the solid phase of the soil. This has to be regarded when forest soils are planned to be fertilized. Alternatively, plants have to assist desorption and dissolution processes of P with the production of exsudates and the promotion of the symbiosis with mycorrhiza.

Furthermore, the study revealed that for the modeling of P transport in forest soils, not only ad- and desorption, but other processes like diffusion to deeper soil layers, precipitation/dissolution and complexation of P should be included into the models that build on the convection dispersion equation. We could show that when parameters form batch experiments were used as input, the model overestimated the sorption of P in four of the six soil samples, whereas in two samples we found the opposite.

The results demonstrate that the behavior of P in the investigated forest soil varied on a small scale. Thus, it would be of interest to further study the relationship between P sorption/desorption and soil properties.

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Deposition and canopy exchange processes of beech forests differing in tree species diversity in Central Germany

U. TALKNER, I. KRÄMER, D. HÖLSCHER & F. O. BEESE

Abstract

Atmospheric deposition of ions is an important nutrient input to forests. The ion composition of rainfall is altered by the forest canopy due to interception and canopy exchange. Bulk deposition and stand deposition (throughfall plus stemflow) of Na^+, Cl^-, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, H^+, Mn^{2+}, Al^{3+}, Fe^{2+}, NH_4^+, NO_3^- and N_{org} were measured in nine deciduous forest plots with different tree species diversity in Central Germany. Interception deposition and canopy exchange rates were calculated with a canopy budget model. The investigated forest plots were pure beech (*Fagus sylvatica* L.) plots, three species plots (*F. sylvatica*, *Tilia cordata* Mill. and/or *T. platyphyllos* Scop. and *Fraxinus excelsior* L.) and five species plots (*F. sylvatica*, *T. cordata* and/or *T. platyphyllos*, *F. excelsior*, *Acer platanoides* L., *A. pseudoplatanus* L. and/or *A. campestre* L. and *Carpinus betulus* L.). The interception deposition of all ions was highest in pure beech plots and was negatively related to the Shannon index. The stand deposition of K^+, Ca^{2+}, Mg^{2+} and PO_4^{3-} was higher in mixed species plots than in pure beech plots. This was due to higher canopy leaching rates in the mixed species plots. The acid input to the canopy as well as to the soil was higher in pure beech plots than in mixed species plots. The high canopy leaching rates of Mn^{2+} in pure beech plots pointed to differences in soil properties between the plot types. Indeed, pH, effective cation exchange capacity and base saturation were smaller in pure beech plots. This may have contributed to the lower leaching rates of K^+, Ca^{2+} and Mg^{2+} compared to the mixed species plots. However, foliar analyses pointed to differences in the ion status between the tree species, which may additionally have influenced canopy exchange. In conclusion, the nutrient input to the soil due to deposition and canopy leaching was higher in mixed species plots than in pure beech plots, whereas the acid input was highest in pure beech plots.

Introduction

Atmospheric deposition of ions is an important nutrient source in forests (e.g., Swank 1984; Lindberg et al. 1986). It is the total ion input to a canopy and can be divided into several fractions (Fig. 1). The deposition of rain, snow and dry particles is independent from the

receptor surface and occurs due to gravitation (Ulrich 1983a). By contrast, the interception of fog and cloud droplets, aerosols and gases depends on the filtering efficiency of the receptor (size, structure and chemical state) (Ulrich 1983a). In the forest canopy, the receptor surface consists of leaves, branches, stems and canopy lichens. The canopy can act as a source or a sink for the deposited ions. The stand deposition is the ion output of the canopy and consists of throughfall and stemflow, which together represent the ion input to the forest floor. The presence of an understory vegetation in the forest alters the stand deposition before it reaches the soil.

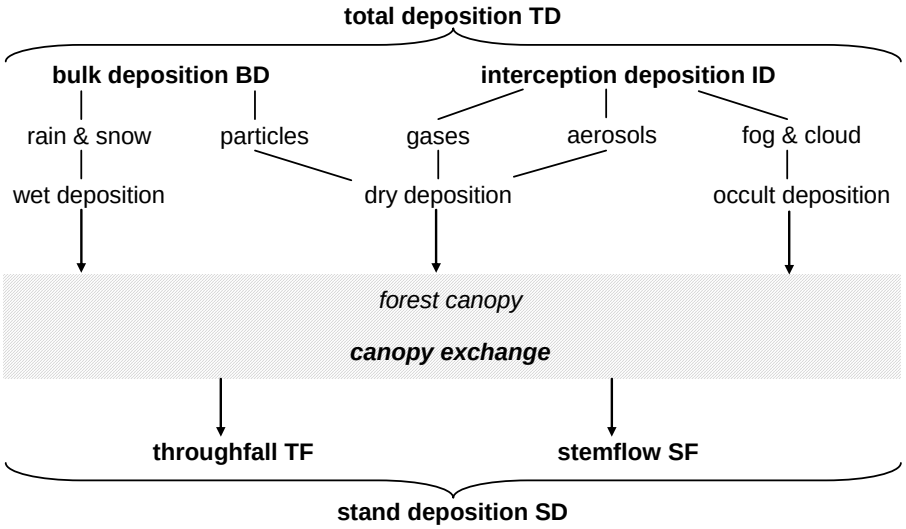

Fig. 1 The deposition inputs and outputs of a forest canopy; the components written in bold were measured or calculated in the present study

Atmospheric deposition is one of the largest nutrient inputs to forest ecosystems. The stand precipitation is a major pathway in nutrient recycling, and the annual nutrient return to the forest soil for potassium, sodium and sulfur is predominantly via stand precipitation and little due to litterfall (Parker 1983). However, deposited acid compounds and heavy metals can negatively influence the trees and the forest soil. This has been shown by many authors in the context of symptoms of forest decline in industrialized countries (e.g., Ulrich and Pankrath 1983; Georgii 1986; Johnson and Lindberg 1992; de Vries et al. 2001; Elling et al. 2007).
Several models have been developed to estimate interception deposition and canopy exchange on the basis of stand deposition and bulk or wet-only deposition measurements, e.g., the regression model from Lovett and Lindberg (1984) and the canopy budget models from Ulrich (1983a) and Beier et al. (1992). In the present study the canopy budget model from Ulrich (1983a; 1994) was used to estimate interception deposition and canopy exchange. Draaijers and Erisman (1995) compared the deposition estimates of the canopy budget model

from Ulrich (1983a) with estimates derived from micrometeorological measurements and inferential modeling and got similar results, with deposition of NO_x being the only exception.
Besides abiotic factors, the interception deposition depends on the leaf area, the physical and chemical properties of the leaf surface and the structural properties of the canopy (Erisman and Draaijers 2003; André et al. 2008). It increases, for example, with increasing stand height and canopy roughness (Erisman and Draaijers 2003). The exchange processes in the canopy comprise uptake and leaching of ions and depend on the physiology and ion status of the trees and the ion permeability of leaves (Draaijers et al. 1994; André et al. 2008). European beech (*Fagus sylvatica* L.) trees are known to have lower leaf ion concentrations than for example European hornbeam (*Carpinus betulus* L.) and small-leaved lime (*Tilia cordata* Mill.) (Krauß and Heinsdorf 2005). Hence, different tree species may affect interception and canopy exchange processes differently. Indeed, several studies have shown stand deposition to be significantly influenced by tree species composition (Potter et al. 1991; Draaijers et al. 1992; Lovett et al. 1996).
Because of changes in forest management, tree species diversity is increasing in German forests (Baumgarten and von Teuffel 2005; Knoke et al. 2005). However, it is not fully understood and quantified how the alteration in tree species composition affects nutrient cycling in forests. Hence, it is of interest to gain insight into the deposition and canopy exchange processes in mixed compared to single species stands (e.g., Nordén 1991; Berger et al. 2008).
We conducted an observational study in a temperate deciduous old-growth forest in Central Germany in order to gain insights into the effects of tree species composition on deposition and canopy exchange processes. In contrast to observational studies, experiments in synthetic forest stands minimize the differences in soil properties and include all relevant treatments (monospecific plots of each tree species and all possible mixtures). However, planted synthetic stands often differ from natural forests in several respects, including trophic structure, tree age distribution and horizontal and vertical canopy structure (Leuschner at al. 2009). Furthermore, edge effects may interfere with species effects and a quasi-steady state in soil development is mostly lacking. Thus, experiments in planted synthetic stands should be combined with observational studies in existing forest stands differing in tree species diversity.
The present observational study aims at investigating the differences in ion input to the canopy with bulk and interception deposition, the canopy exchange processes as well as the ion output from the canopy with throughfall and stemflow along a tree species diversity

gradient from monospecific beech plots to deciduous tree species rich plots in Central Germany.

Materials and methods

Study site

The study site (51°5'N, 10°30'E) is located in Central Germany in the Hainich National Park. The typical vegetation types of the National Park are beech and deciduous mixed-beech forests. Since 1990 the forest has not been managed, and has only been used for recreation. From the 1960s to 1990 the area was used for military training. For the last 40 years, only single stems have been extracted from the forest and it regenerated naturally. The area has been covered by deciduous forest for at least 200 years. Thus, it represents an old-growth forest with respect to stand continuity in the definition of Wulf (2003) (Schmidt et al. 2009). The National Park is surrounded by deciduous forest, agricultural land and small villages. The nearest city (Erfurt) with more than 200,000 inhabitants is about 50 km away from the National Park in south-eastern direction.

Nine study plots (each 0.25 ha) with differing tree species diversity were selected within a radius of approximately 5 km in the north-eastern part of the Hainich National Park. The selected forest plots were located in a contiguous forest area. Each forest plot could be assigned to one of three tree species diversity levels (DL). DL1: the tree layer constitutes to at least 95 % of beech (*Fagus sylvatica* L.); DL2: the tree layer constitutes to at least 95 % of beech, lime (*Tilia cordata* Mill. and/or *T. platyphyllos* Scop.) and ash (*Fraxinus excelsior* L.); DL3: the tree layer constitutes to at least 95 % of beech, lime, ash, maple (*Acer platanoides* L., *A. pseudoplatanus* L. and/or *A. campestre* L.) and hornbeam (*Carpinus betulus* L.).

Three replicate plots were selected for each diversity level. The forest plots of DL1 are hereafter referred to as "pure beech plots" and the forest plots of both DL2 and DL3 as "mixed species plots". The tree species composition in the Hainich National Park is largely a result of former forest management. Different ownership and management goals have created a small-scale mosaic of forest stands differing in tree species diversity with pure beech stands growing in close neighborhood of species rich forests with ash, lime, hornbeam, maple and beech. The practice of selective cutting (Plenterwald) or coppicing with standards (Mittelwald), which foster species-rich stands, most likely was associated with a higher disturbance regime for the past 150 to 200 years than the management of beech in age-class

forests (Schmidt et al. 2009). The average age of the trees is 148, 85 and 100 years in the DL1, DL2 and DL3 plots, respectively (Schmidt et al. 2009).

In the studied forest stands, trees began to foliate in early April and foliation was completed in the second half of May. Fully developed foliation in summer remained until the beginning of September when leaf shedding started. The trees were leafless from December to beginning of April.

The mean annual precipitation of the observation period (2005 to 2007) measured at the nearest meteorological station "Weberstedt/Hainich" (51°10'N, 10°52'E; 270 m a.s.l.) was 652 mm (meteomedia GmbH). The mean annual temperature is 7.5°C. The study plots are located at a mean altitude of 340 m a.s.l., have a mean slope of 3.1° and the exposition of all plots is north-east. The bedrock of the Hainich National Park is Triassic limestone covered with a loess layer of different depth. The soil type is a Luvisol (FAO 1998). The soil texture of the loess layer is loamy to clayey silt and in the lower parts of the profile silty clay. The soils of the pure beech plots had lower base saturation (BS), effective cation exchange capacity (CEC_e) and pH than the mixed species plots (Table 1) (Guckland et al. 2009).

DL		BS (%)	CEC_e (mmol(+) kg^{-1})	pH_{H2O}
DL1	$\bar{x}$	**19**	**73**	**4.2**
	s	4	13	0.2
DL2	$\bar{x}$	**79**	**120**	**5.1**
	s	6	43	0.1
DL3	$\bar{x}$	**84**	**153**	**5.3**
	s	11	56	0.2

Table 1 Mean values ($\bar{x}$) and standard deviations (s) of base saturation (BS), effective cation exchange capacity (CEC_e) and pH in the mineral topsoil (0-10 cm) for each diversity level (DL1, DL2, DL3); N=3 (Guckland et al. 2009)

As a measure of diversity, the Shannon diversity index was used (H_0, Shannon and Weaver 1949). H_0 is one of the most common measures for species diversity and depends not only on the number of species present in an ecosystem, but also on their relative abundance (Magurran 2004). In the study area, *Tilia cordata* and *T. platyphyllos* often hybridized. Hence, in the calculation of the Shannon index, *T. cordata* and *T. platyphyllos* were considered as one species. For stand height, the average height of the 20% highest trees was taken (tree height: M. Jacob, pers. comm.). Canopy roughness was defined by the height difference between the mean height of the 10% highest and 10% smallest trees. The leaf area index (LAI; leaf area in m^2 m^{-2}) of the study plots was determined based on leaf biomass (Jacob et al. in press).

Therefor, litter traps were placed next to the precipitation collectors (see section "Rain water sampling and chemical analyses") and emptied several times during autumnal leaf shedding. Leaves of all species were scanned and the leaf area was analyzed using WinFOLIA (Regent Instruments, Canada). Subsequently, all leaves were dried and weighed and the specific leaf area (SLA) was calculated. The LAI was obtained by multiplying the stand leaf biomass of each species with the species-specific average of SLA (Jacob et al. in press). The main differences in the forest stand characteristics of the tree layer were found between the pure beech plots and the mixed species plots (Table 2). The characteristics of the mixed species plots of DL2 did not differ substantially from those of DL3.

DL		Shannon index	Stand height[a]	Canopy roughness[b]	LAI[c]
			(m)		(m^2 m^{-2})
DL1	$\bar{x}$	**0.27**	**38**	**26**	**6.4**
	s	0.26	2.7	7.4	0.6
DL2	$\bar{x}$	**1.00**	**31**	**20**	**6.9**
	s	0.18	1.3	1.5	0.4
DL3	$\bar{x}$	**1.25**	**29**	**18**	**7.1**
	s	0.04	0.5	0.8	0.2

Table 2 Mean values ($\bar{x}$) and standard deviations (s) of the forest stand characteristics for each diversity level (DL1, DL2, DL3); N=3.

[a] M. Jacob, pers. comm.

[b] Krämer and Hölscher 2009.

[c] Jacob et al. in press; the mean values of the leaf area index (LAI) of three years (2005, 2006, 2007) are presented

Rain water sampling and chemical analyses

The following portions of the rain water were sampled every two weeks: bulk precipitation, throughfall and stemflow. Bulk precipitation was sampled at four sites outside the forest, each with three continuously open precipitation collectors. At each site, the three collectors were placed in a triangle with a side length of 2 m. The sites were located about 50 m from the forest edge, and the distance to the selected forest plots ranged from 200 m to 1200 m. For the chemical analyses, the water of the three precipitation collectors of each site was pooled, resulting in four replicate samples per date for the bulk precipitation. Throughfall was sampled with a total of 15 throughfall collectors in each forest plot. The collectors were situated along three randomly selected 30 m long transects with five collectors along each transect. The collector positions along transects were defined randomly with a minimum

distance of 4 m between two collectors. For the chemical analyses, the water of the five throughfall collectors of each transect was pooled, resulting in three replicate samples per forest plot and date for the throughfall. The collectors used for bulk precipitation and throughfall sampling were placed at a height of 1 m and had a diameter of 10.5 cm. They were opaque in order to prevent the growth of algae. In winter, snow was sampled with buckets. The diameter of the buckets was 25 cm and the sampling design the same as during the rest of the year. The stemflow was sampled adjacent to the selected forest plots at a total of 50 trees representing the tree species and the diameter classes found in the forest plots. All stemflow samples were analyzed chemically. The stemflow volume per plot was calculated based on species-specific regressions between the diameter at breast height (dbh) and stemflow volume per measuring period, combined with stem number and dbh of the trees on the study plots. When there was no persistent correlation between dbh and stemflow for a certain species (ash, lime and sycamore), an average value of the stemflow volume of all measured trees of this species was taken. The ion concentration was multiplied by the water volume of each sample, resulting in the ion mass per sample. For each tree species the median of the ion mass was calculated and divided by the water volume per tree species, resulting in the ion concentration per tree species. This ion concentration was finally multiplied by the water volume per plot and upscaled to one hectare, resulting in the ion mass per hectare (kg ha^{-1}) for the stemflow.

Bulk precipitation and throughfall were sampled manually every two weeks during a two-year period from July 2005 through June 2007. Stemflow was sampled manually every two weeks during a one-year period from July 2006 through June 2007. For further details on the water sampling see Krämer and Hölscher (2009).

The water samples were filtered through a Whatman filter paper 589/1 with a pore size of 12-25 µm and stored at 3 °C before chemical analyses. The ions Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, H^{+}, Mn^{2+}, Al^{3+} and Fe^{2+} were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Spectro, Kleve, Germany). Cl^{-} was measured potentiometrically and N compounds photometrically, both with an automated continuous-flow analyzer (Skalar Analytic GmbH, Breda, The Netherlands). C compounds were measured by an automated carbon analyzer (Shimadzu TOC-5050, Duisburg, Germany).

Canopy budget model

This section briefly describes the canopy budget model that we used for calculating interception deposition, total deposition and canopy exchange. For more detailed explanations

we refer to Ulrich (1983a; 1994) and Bredemeier (1988). The total atmospheric deposition (TD) of an ecosystem is the sum of the precipitation deposition and the interception deposition (ID); the latter can be gaseous (ID_{gas}) or particulate (ID_{part}). We used bulk precipitation collectors outside the forest to measure precipitation deposition. Hence, we did not measure wet-only, but bulk deposition (BD) (Eq. [1]).

$$TD = BD + ID \quad [1]$$

The stand deposition (SD) is the sum of the deposition with throughfall (TF) and stemflow (SF), which were both measured in the field (Eq. [2]).

$$SD = TF + SF \quad [2]$$

Leaves, branches and stems can act as sinks or sources of ions for the water passing through the canopy (throughfall) and along the stem (stemflow). This canopy exchange (CE) can be described by the difference between total deposition (TD) and stand deposition (SD) (Eq. [3]).

$$CE = TD - SD = BD + ID - SD \quad [3]$$

The difference can either be positive, which means that the canopy acts as a sink and the ion is taken up by the canopy, or negative, which means that the canopy acts as a source and the ion is leached from the canopy. Several processes contribute to the sink function of the forest canopy: assimilation (NH_4^+, NO_3^-) (Boynton 1954; Matzner 1986), cation exchange in the leaf tissue (exchange of H^+ against Ca^{2+} and Mg^{2+}) (Ulrich 1983b; Roelofs et al. 1985), storage of particles (Al^{3+}, heavy metals) and precipitation of dissolved ions (Al^{3+}, heavy metals) (Godt 1986). Other processes contribute to the source function of the forest canopy: leaching of ions from senescent leaves mainly in autumn (Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}) (Ulrich 1983a), leaching of ions throughout the growing season due to metabolic processes (K^+, Mn^{2+}) (Ulrich 1983a), cation exchange in the leaf tissue (exchange of K^+, Ca^{2+}, Mg^{2+} against H^+ or NH_4^+) (Ulrich 1983a; b; Stachurski and Zimka 2002), simultaneous leaching of cations (K^+, Ca^{2+}, Mg^{2+}) and weak acids (e.g., weak organic anions, bicarbonate) (Draaijers and Erisman 1995; Chiwa et al. 2004) and dissolution of undissolved matter in deposited particles (Al^{3+}, heavy metals) (Mayer 1983). It is often supposed by some authors that Na^+, Cl^-, SO_4^{2-} and NO_3^- are neither leached from nor taken up by the forest canopy (Lindberg et al. 1986; Matzner 1986; Ulrich 1994; Draaijers and Erisman 1995). However, others state that there is canopy leaching of Na^+, Cl^- and SO_4^{2-} and canopy uptake of NO_3^- (Staelens et al. 2008). It may be assumed that leaching is negligible for those ions whose ratio of SD to BD is constant throughout the year. In the present study this was the case for Na^+, but not for Cl^-, SO_4^{2-} and NO_3^-. Therefore, we set the CE of Na^+ to zero and used it as a tracer ion for the calculation of particulate interception deposition of several other ions. One major assumption of the canopy budget

model is that the interception rate depends on the precipitation deposition (in our case BD) and not on the ion. Because Na^+ is not exchanged in the canopy and does not exist in gaseous form, the particulate interception deposition (ID_{part}) can be calculated directly from SD and BD according to Eq. [3]. The ratio of ID_{part} to BD for Na^+ was then used to calculate ID_{part} of the ions Cl^-, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, H^+, Mn^+, Al^{3+}, Fe^{2+}, NH_4^+ and NO_3^-. The assumption that particles containing these elements are deposited with the same efficiency as Na^+ containing particles might not be true (Draaijers et al. 1997); however, the error introduced by this assumption is probably the same for all study plots since they are located in one coherent forest area. Thus, it is possible to compare interception deposition and canopy exchange between the study plots. The ions Cl^-, SO_4^{2-}, H^+, NH_4^+ and NO_3^- may also be deposited as gases (ID_{gas}). Since it was not possible to estimate ID_{gas}, the total deposition and the canopy uptake of these ions might be underestimated and the canopy leaching overestimated.

The canopy leaching of K^+, Ca^{2+} and Mg^{2+} is supposed to be accompanied by the uptake of H^+ and NH_4^+ or the leaching of weak acids. Thus, the canopy exchange of H^+ and NH_4^+ can be calculated by subtracting the leaching of K^+, Ca^{2+} and Mg^{2+} from the leaching of weak acids (Draaijers and Erisman 1995; Staelens et al. 2008). The amount of weak acids in BD and SD can be calculated from the cation-anion balance (Draaijers and Erisman 1995; Staelens et al. 2008). To separate the uptake of H^+ and NH_4^+ a relative uptake efficiency factor is normally used. However, this factor is tree-species specific (Staelens et al. 2008) and has not been determined for beech or any of the other tree species present in the study plots. Thus, we did not use this approach. De Vries et al. (2001) suggested a method for calculating the canopy uptake of NO_3^-. Since this approach is dependent on the uptake of NH_4^+ and again an efficiency factor for the uptake of NH_4^+ vs. NO_3^- has to be used, we considered this calculation to be too unreliable.

The acid input to the forest canopies was calculated as the sum of the total deposition (TD) of the cations H^+, Mn^{2+}, Al^{3+}, Fe^{2+} and NH_4^+ (Ulrich 1994). The acid buffering capacity of the canopies was calculated as the sum of the positive canopy exchange (CE), that is, the uptake of the cations H^+, Mn^{2+}, Al^{3+}, Fe^{2+} and NH_4^+ (Ulrich 1994).

Data analyses and statistics

The ion concentrations of bulk precipitation, throughfall and stemflow were checked for outliers. These outliers were identified by very high carbon, nitrogen, phosphorus or potassium contents. In total, 40 out of 1060 data points (i.e., less than 4%) were removed

from the dataset before doing any calculations. Since we had three pooled samples per study plot and date and we never had to remove all of them, the deletion of single data points still allowed the calculation of annual budgets.

The chemical analyses of the bulk precipitation samples revealed that the four sites outside the forest had a large variation in ion composition among the sampling dates and the sites, but there were no directed differences between the four sites. Hence, the sites were regarded as replicates for the bulk precipitation and mean values of the four replicate sites were calculated.

For each forest plot mean values per sampling date were calculated from the three pooled throughfall samples per plot. These mean values of the three replicate forest plots of each diversity level were used for further calculations and statistical analyses, because the forest plots are our true replicates. The mean values for each date of the two years measured were summed up resulting in annual precipitation and throughfall fluxes. The mean value of the two annual fluxes was calculated to smooth annual fluctuations.

The stemflow data were also summed up to reveal a one-year sum. To estimate the sum of the first year (July 2005 to June 2006), for which no stemflow data were available, the ratio of stemflow to throughfall for each plot and chemical compound of the second year (July 2006 to June 2007) was calculated and multiplied with the throughfall for each plot and chemical compound of the first year. Again, the mean value of the two annual fluxes was calculated to smooth annual fluctuations.

The two-year means of the throughfall and stemflow data were summed up to reveal the stand deposition. The two-year means of the bulk deposition (BD) and the stand deposition (SD) were used to calculate the interception deposition (ID), the total deposition (TD) and the canopy exchange (CE) of each plot and chemical compound as described above (see section "Canopy budget model").

The aim of this study was to evaluate differences in the ID, TD, CE and SD between the diversity levels and along the tree species diversity gradient. Therefore, the two-year means of the ID, TD, CE and SD of every chemical compound were used as dependent variables in an analysis of variance (ANOVA) with the diversity level as the explaining variable. Differences between the diversity levels were deemed to be significant when they exceeded the least significant difference, LSD, computed for every pair of diversity levels ($p<0.05$). In addition, ID, TD, CE and SD of each plot and chemical compound were used in a multiple linear regression model with the Shannon index and the leaf area index (LAI) as explaining variables. The ANOVA with diversity level as explaining variable and the multiple linear

regression model with Shannon index and LAI as explaining variables are different approaches to elucidate the influence of the tree species composition on deposition and canopy exchange.

All statistical analyses were done with R version 2.7.2 (R Development Core Team 2007).

Results

Forest stand characteristics

The investigated forest plots differed in their stand characteristics (Table 2). Pure beech plots (i.e., lowest Shannon index) were higher and had rougher canopies than mixed species plots. Shannon index, stand height and canopy roughness correlated significantly with one another, whereas LAI only correlated with stand height (Table 3).

Since most of the stand characteristics were linearly correlated, the effects of single stand characteristics on the canopy deposition and exchange processes could not be isolated. We used the Shannon index as a measure for the correlated stand characteristics and the LAI as an additional stand characteristic in a multiple linear regression model to explain differences in interception deposition, canopy exchange and stand deposition.

variable 1	variable 2	p	r
Shannon index	stand height	**<0.001 *****	**-0.97**
Shannon index	canopy roughness	**0.003 ****	**-0.86**
Shannon index	LAI	0.09	0.59
stand height	canopy roughness	**0.004 ****	**0.84**
stand height	LAI	**0.04 ***	**-0.69**
canopy roughness	LAI	0.30	-0.39

Table 3 P-values and correlation coefficients of the Pearson's product-moment correlations with stand characteristics as variables; * $0.01 \leq p < 0.05$, ** $0.001 \leq p < 0.01$, *** $p < 0.001$

Variations in ion fluxes

During the course of the year the ratio of SD to BD was constant for Na^+, whereas this ratio was much larger in summer and autumn than during the rest of the year for the ions K^+, Ca^{2+}, Mg^{2+} and to a lesser extent also for Cl^-, PO_4^{3-}, SO_4^{2-} and NO_3^-. This indicates that Na^+ was not exchanged by the canopy, whereas the other ions were leached from the canopy during summer and autumn, leading to the seasonal variations.

The amount of stemflow was very low compared to the amount of bulk precipitation and throughfall (0.4% to 4.9% of bulk precipitation) (Krämer and Hölscher 2009); hence, the ion

fluxes were generally also very low. The stemflow fluxes of the ions were on average 3.7% of the throughfall fluxes, with H^+ having the lowest percentage (0.2%) and Al^{3+} having the highest (17.6%). Stemflow fluxes did not differ between the diversity levels.

Deposition and canopy exchange

Total and interception deposition of all ions were significantly decreasing with increasing diversity level (ANOVA) and were negatively related to the Shannon index but not related to the LAI (multiple linear regression model; adjusted R^2=0.86, Shannon index: p<0.001***, LAI: p=0.10). The interception deposition was calculated in the same way for all ions. Hence, the differences in interception deposition between the diversity levels were the same for all ions. Since the total deposition is the sum of bulk deposition and interception deposition and the bulk deposition is the same for all diversity levels, the differences between the diversity levels in total deposition were the same as those in interception deposition.

The ion Na^+ was neither taken up by nor leached from the canopy in the study plots. Most of the other ions were leached from the canopy (Table 4). Only NH_4^+ was taken up in all investigated forest plots and H^+ ions were taken up in the mixed species plots and leached in the pure beech plots. The results of the ANOVA showed that the canopy exchange rates of most of the ions were different in pure beech compared to mixed species plots, only the exchange rates of Al^{3+}, NH_4^+, and NO_3^- were comparable in all investigated forest plots. The canopy leaching of Cl^-, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, and Fe^{2+} increased with increasing diversity level. On the other hand, the leaching of Mn^{2+} was largest in the pure beech plots. The multiple linear regression model revealed that the exchange rates of Mg^{2+}, PO_4^{3-}, SO_4^{2-}, Al^{3+}, Fe^{2+}, NH_4^+ and NO_3^- were not related to the Shannon index (Table 5). The leaching of Cl^-, K^+ and Ca^{2+} was related positively and the leaching of Mn^{2+} was related negatively to the Shannon index (Table 5 and Fig. 2). The canopy exchange rates of all ions were not related to the LAI.

Accordingly, the stand deposition of Na^+, Cl^-, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, Fe^{2+} and N_{org} was larger in mixed species plots than in pure beech plots, whereas the stand deposition of H^+, Mn^{2+} and NH_4^+ was largest in pure beech plots, and did not differ between the diversity levels for SO_4^{2-}, Al^{3+}, NO_3^- and N_t. For K^+ and Ca^{2+}, SD was positively and for Na^+, H^+, Mn^{2+}, NH_4^+, NO_3^- and N_t negatively related to the Shannon index (Table 5). The stand deposition of Cl^-, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, Al^{3+}, Fe^{2+} and N_{org} was not related to the Shannon index. Only the SD of NO_3^- was positively related to the LAI.

		H_2O	Na^+	Cl^-	K^+	Ca^{2+}	Mg^{2+}	PO_4^{3-}-P	SO_4^{2-}-S	H^+	Mn^{2+}	Al^{3+}	Fe^{2+}	NH_4^+-N	NO_3^--N	N_{org}	N_t
		(mm)	(kg ha^{-1} a^{-1})														
BD	$\bar{x}$	**614**	**3.27**	**4.77**	**2.45**	**3.47**	**0.48**	**0.44**	**2.69**	**0.065**	**0.010**	**0.011**	**0.033**	**6.33**	**6.07**	**1.41**	**13.8**
	s	77	0.74	1.20	1.40	0.98	0.16	0.47	0.63	0.044	0.012	0.016	0.024	4.83	3.45	0.82	8.1
ID DL1	$\bar{x}$	**168**	**0.76**	**1.11**	**0.57**	**0.81**	**0.11**	**0.10**	**0.63**	**0.015**	**0.002**	**0.003**	**0.008**	**1.48**	**1.42**	**n.d.**	**n.d.**
	s	21	0.21	0.30	0.15	0.22	0.03	0.03	0.17	0.004	0.001	0.001	0.002	0.40	0.38	n.d.	n.d.
ID DL2	$\bar{x}$	**136**	**0.39**	**0.57**	**0.29**	**0.42**	**0.06**	**0.05**	**0.32**	**0.008**	**0.001**	**0.001**	**0.004**	**0.76**	**0.73**	**n.d.**	**n.d.**
	s	29	0.08	0.12	0.06	0.09	0.01	0.01	0.07	0.002	0.000	0.000	0.001	0.16	0.15	n.d.	n.d.
ID DL3	$\bar{x}$	**165**	**0.26**	**0.38**	**0.19**	**0.27**	**0.04**	**0.03**	**0.21**	**0.005**	**0.001**	**0.001**	**0.003**	**0.50**	**0.48**	**n.d.**	**n.d.**
	s	44	0.16	0.24	0.12	0.17	0.02	0.02	0.13	0.003	0.000	0.001	0.002	0.31	0.30	n.d.	n.d.
TD DL1	$\bar{x}$	**614**	**4.04**	**5.88**	**3.02**	**4.28**	**0.59**	**0.55**	**3.32**	**0.081**	**0.012**	**0.013**	**0.040**	**7.81**	**7.48**	**n.d.**	**n.d.**
	s	77	0.21	0.30	0.15	0.22	0.03	0.03	0.17	0.004	0.001	0.001	0.002	0.40	0.38	n.d.	n.d.
TD DL2	$\bar{x}$	**614**	**3.67**	**5.34**	**2.74**	**3.89**	**0.54**	**0.50**	**3.02**	**0.073**	**0.011**	**0.012**	**0.037**	**7.09**	**6.80**	**n.d.**	**n.d.**
	s	77	0.08	0.12	0.06	0.09	0.01	0.01	0.07	0.002	0.000	0.000	0.001	0.16	0.15	n.d.	n.d.
TD DL3	$\bar{x}$	**614**	**3.53**	**5.14**	**2.64**	**3.75**	**0.52**	**0.48**	**2.91**	**0.070**	**0.011**	**0.012**	**0.035**	**6.83**	**6.54**	**n.d.**	**n.d.**
	s	77	0.16	0.24	0.12	0.17	0.02	0.02	0.13	0.003	0.000	0.001	0.002	0.31	0.30	n.d.	n.d.
CE DL1	$\bar{x}$	**n.d.**	**0**	**-2.52**	**-12.43**	**-1.30**	**-0.67**	**-0.18**	**-0.75**	**-0.006**	**-0.408**	**-0.002**	**-0.005**	**1.55**	**-2.80**	**n.d.**	**n.d.**
	s	n.d.	0	0.15	1.33	0.71	0.18	0.27	0.08	0.004	0.116	0.015	0.002	0.53	0.57	n.d.	n.d.
CE DL2	$\bar{x}$	**n.d.**	**0**	**-3.56**	**-19.35**	**-3.57**	**-0.99**	**-0.40**	**-1.39**	**0.015**	**-0.105**	**-0.004**	**-0.013**	**2.38**	**-2.79**	**n.d.**	**n.d.**
	s	n.d.	0	0.59	0.99	0.52	0.16	0.21	0.29	0.006	0.008	0.006	0.003	0.42	0.39	n.d.	n.d.
CE DL3	$\bar{x}$	**n.d.**	**0**	**-4.54**	**-22.72**	**-4.86**	**-1.43**	**-0.98**	**-1.54**	**0.019**	**-0.078**	**-0.008**	**-0.026**	**1.80**	**-3.02**	**n.d.**	**n.d.**
	s	n.d.	0	0.55	2.14	0.59	0.25	0.15	0.54	0.011	0.031	0.006	0.008	0.99	0.77	n.d.	n.d.
SD DL1	$\bar{x}$	**446**	**4.04**	**8.40**	**15.45**	**5.58**	**1.26**	**0.73**	**4.07**	**0.086**	**0.420**	**0.015**	**0.046**	**6.26**	**10.28**	**1.35**	**17.9**
	s	21	0.21	0.20	1.46	0.75	0.18	0.30	0.21	0.009	0.116	0.015	0.001	0.86	0.95	0.10	1.8
SD DL2	$\bar{x}$	**478**	**3.67**	**8.91**	**22.09**	**7.46**	**1.52**	**0.90**	**4.41**	**0.058**	**0.117**	**0.016**	**0.050**	**4.71**	**9.58**	**1.48**	**15.8**
	s	29	0.08	0.49	0.93	0.46	0.16	0.20	0.24	0.008	0.008	0.005	0.002	0.54	0.46	0.01	1.0
SD DL3	$\bar{x}$	**449**	**3.53**	**9.68**	**25.36**	**8.60**	**1.95**	**1.46**	**4.44**	**0.052**	**0.089**	**0.020**	**0.062**	**5.03**	**9.56**	**1.66**	**16.3**
	s	44	0.16	0.32	2.11	0.47	0.24	0.13	0.46	0.008	0.032	0.005	0.009	0.69	0.55	0.06	1.2

Table 4 Mean values ($\bar{x}$) and standard deviations (s) of the annual water and ion fluxes with bulk deposition (BD), interception deposition (ID), total deposition (TD), canopy exchange (CE) and stand deposition (SD) for each diversity level (DL1, DL2, DL3); BD (N=4) and SD (N=3) were measured in the field; ID (N=3), TD (N=3) and CE (N=3) were calculated with the canopy budget model (Ulrich 1983; Ulrich 1994); n.d. = not determined

		canopy exchange		stand deposition	
		p	adj. R^2	p	adj. R^2
Na^+	Shannon index	-	-	**<0.001 *** **	**0.86**
	LAI	-		0.10	
Cl^-	Shannon index	**0.02 ***	**0.57**	0.12	0.30
	LAI	0.77		0.88	
K^+	Shannon index	**0.01 ***	**0.69**	**0.02 ***	**0.67**
	LAI	0.93		0.89	
Ca^{2+}	Shannon index	**0.01 ***	**0.72**	**0.03 ***	**0.66**
	LAI	0.67		0.50	
Mg^{2+}	Shannon index	0.10	0.46	0.14	0.41
	LAI	0.55		0.47	
PO_4^{3-}-P	Shannon index	0.23	0.57	0.35	0.54
	LAI	0.12		0.10	
SO_4^{2-}-S	Shannon index	0.06	0.35	0.35	-0.11
	LAI	0.55		0.81	
H^+	Shannon index	**0.02 ***	**0.57**	**0.003 ****	**0.78**
	LAI	0.70		0.41	
Mn^{2+}	Shannon index	**0.003 ****	**0.83**	**0.003 ****	**0.83**
	LAI	0.56		0.57	
Al^{3+}	Shannon index	0.99	-0.33	0.85	-0.32
	LAI	0.97		0.93	
Fe^{2+}	Shannon index	0.06	0.48	0.23	0.24
	LAI	0.77		0.60	
NH_4^+-N	Shannon index	0.45	-0.19	**0.03 ***	**0.44**
	LAI	0.78		0.43	
NO_3^--N	Shannon index	0.37	0.15	**0.004 ****	**0.70**
	LAI	0.12		**0.02 ***	
N_{org}	Shannon index	-	-	0.15	0.57
	LAI	-		0.18	
N_t	Shannon index	-	-	**0.02 ***	**0.50**
	LAI	-		0.11	

Table 5 P-values and adjusted coefficients of determination (adj. R^2) of multiple linear regression models with Shannon index and LAI as explaining variables for the variance in canopy exchange and stand deposition of every chemical compound; * $0.01 \leq p < 0.05$, ** $0.001 \leq p < 0.01$, *** $p < 0.001$

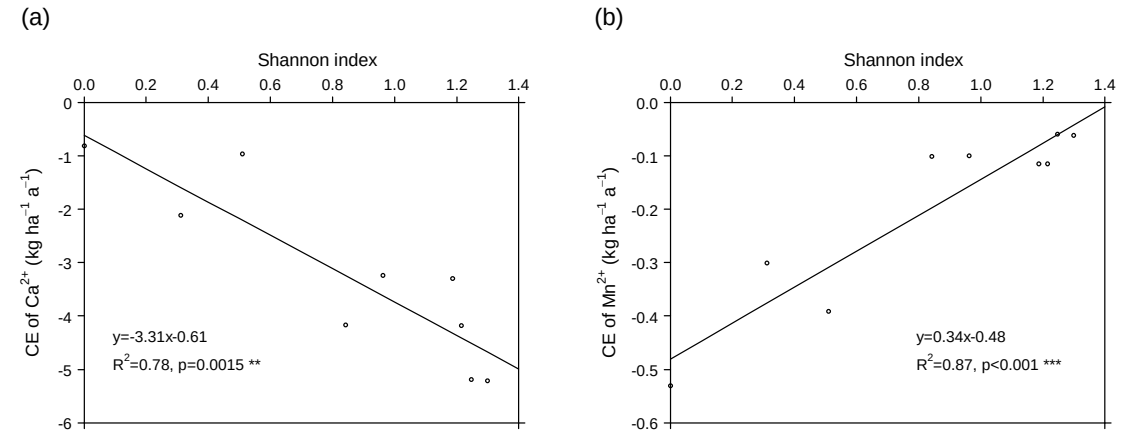

Fig. 2 Relation between the canopy exchange (CE) of Ca^{2+} (a) and Mn^{2+} (b), respectively, and the Shannon index; the linear equations, the coefficients of determination (R^2) and the p-values are given; N=9

The acid input to the canopies of the study plots decreased with increasing diversity level (Fig. 3) and was negatively related to the Shannon index but not to the LAI (adjusted R^2=0.86, Shannon index: p<0.001***, LAI: p=0.10). However, the acid buffering capacity of the canopies did not differ significantly between the diversity levels and was neither related to the Shannon index nor to the LAI (adjusted R^2=-0.19, Shannon index: p=0.44, LAI: p=0.79).

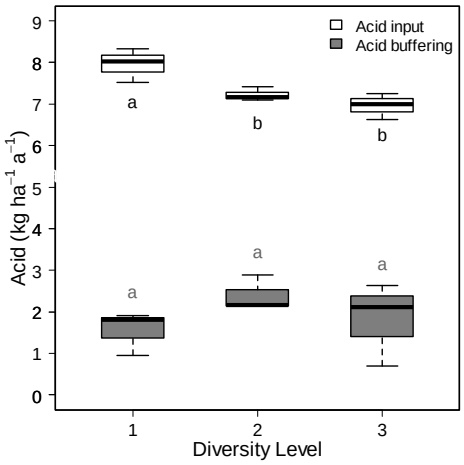

Fig. 3 Acid input and acid buffering capacity of the forest canopy for each diversity level (DL1, DL2, DL3); N=3

Discussion

Comparison of deposition with other data

In Germany, the fluxes of Na^+ and Cl^- with precipitation decrease with increasing distance to the North Sea. This decrease is more pronounced in stand deposition than in bulk deposition, indicating that interception of seaborne particles decreases rapidly with increasing distance

from the shore (Bredemeier 1988). The molar ratio of Na^+ to Cl^- is 0.86 in sea water. In the studied forest plots it was 1.08 for bulk deposition and 0.56 to 0.74 for stand deposition. This is in accordance with other studies (Bredemeier 1988; Nordén 1991). Since Na^+ is not exchanged in the canopy (see next paragraph) and may be considered as solely derived from atmospheric sea salt deposition (Ulrich 1983a), the deviations of the measured ratios from the ratio in sea water have to be due to relatively more Cl^- in the stand precipitation than in sea water. In addition, the ratio was decreasing with increasing diversity level. This can be explained by increasing canopy leaching rates for Cl^- with increasing diversity level (see section "Differences in interception deposition and canopy exchange between the diversity levels").

The usage of Na^+ as a tracer ion to calculate particulate interception deposition of other ions requires that Na^+ is not exchanged in the canopy. However, canopy leaching of Na^+ during the short period of leaf emergence is reported (Staelens et al. 2007). If ions are exchanged in the canopy, seasonal differences in the ratio of SD to BD can be observed. For Na^+, this ratio differed among sampling dates but neither among seasons nor among plots. In contrast, the SD to BD ratio showed seasonal differences for the other ions that are often supposed to behave inert in the canopy: Cl^-, SO_4^{2-} and NO_3^-. Thus, we concluded that Na^+ was not exchanged and hence, can be used as a tracer ion in the canopy budget model. For the other ions, canopy exchange was considered.

Compared with the total deposition of other German beech forests in the year 2002, the total deposition reported in the present study is about the same for K^+ and 80% and 90% lower for Mg^{2+} and Ca^{2+}, respectively (Meesenburg et al. 2009). The bulk and stand deposition of PO_4^{3-} were 80% to 95% higher in the investigated forest plots compared with deciduous mixed forests in Southern Sweden (Nordén 1991). In contrast, the bulk and stand deposition of SO_4^{2-} were 80% to 90% lower in the investigated forest plots compared with German beech forests in the 1980s (Bredemeier 1988). This is in accordance with the reduced sulfur deposition in Germany during the last decades (Meesenburg et al. 1995; Ulrich et al. 2006). Even compared with more recent data of similar German beech forests, the sulfur deposition of the investigated forest plots is more than 90% lower (Meesenburg et al. 2009). This could be explained by the remote location of our forest plots. The stand and total deposition of H^+ and Mn^{2+} were 80% to 90% lower and those of NH_4^+ 50% to 60% lower in our study than reported in Nordén (1991), Matzner and Meiwes (1994) and Meesenburg et al. (2009), indicating a reduction of acid emissions and the remote location of the study site. The stand deposition of NO_3^- was about the same as reported in Matzner and Meiwes (1994) and the

total deposition about 80% lower than reported in Meesenburg et al. (2009). Only small amounts of the total N deposited with throughfall were in organic form (8% to 10%), whereas Gaige et al. (2007) reported that organic N was more than 80% of N_t in throughfall.

To summarize, total and stand deposition of SO_4^{2-}, H^+, Mn^{2+} and NH_4^+ reported here were much lower than reported in the above mentioned studies, whereas total and stand deposition of K^+, Ca^{2+} and Mg^{2+} were about the same as or also much lower than reported in the above mentioned studies. This is in accordance with the fact that the amount of bulk precipitation of the investigated forest plots was either the same or up to 35% lower than reported in the other studies (Bredemeier 1988; Nordén 1991; Matzner and Meiwes 1994; Meesenburg et al. 2009), which is known to influence the amount of deposition of several ions (Croisé et al. 2005). In addition, not only the reduced emission of sulfur and to a lesser extent nitrogen during the last years, but also the remote location of the study area contributed to the low deposition of sulfur and nitrogen. The Federal Environment Agency of Germany (UBA, 2006) reported values of 4 µg NO_2 per m^3 and 0.9 µg SO_2 per m^3 for June 2006 and a location about 70 km away from the study site, stating that this is a relatively unpolluted area in Germany.

Differences in interception deposition and canopy exchange between the diversity levels

The stand deposition of the investigated ions differed between the diversity levels, with the exceptions being SO_4^{2-}, Al^{3+}, NO_3^- and N_t. Hence, the tree species composition may have influenced the nutrient input to the forest via precipitation (Potter et al. 1991; Draaijers et al. 1992; Lovett et al. 1996). Therefore, we will take a closer look at the processes in the canopy that may explain the observed differences in stand deposition among the forest plots: interception deposition and canopy exchange.

Interception deposition depends on the aerodynamic properties of the receiving surface (Erisman and Draaijers 2003). Properties determined by the canopy as a whole, like canopy roughness, canopy length, canopy cover and LAI, influence the interception deposition, but also properties of individual canopy elements like the efficiency of leaves to capture or absorb gases and particles, or the surface wetness (Erisman and Draaijers 2003). The pure beech plots were highest and had the roughest canopies of the study plots. This may be explained by the former management of the study plots and the tree species present. The beech plots were oldest, and natural regeneration may have led to large height differences leading in turn to the large canopy roughness. Also, the interception deposition of all ions was largest in the pure beech plots and negatively related to the Shannon index. The LAI did not explain any variation in the interception deposition. Since the stand characteristics were correlated, except

for the LAI, it is not possible to isolate which factor contributed most to the differences in interception deposition among the study plots.

To summarize, we can state that the interception deposition decreased along the investigated tree species diversity gradient from monospecific beech plots to tree species rich plots. A significant distinction was found between pure beech plots and mixed species plots, whereas the ion deposition did not differ significantly between the mixed species plots (DL2 and DL3). The same pattern was found for the stand characteristics (except for LAI), which may explain the differences in ion deposition along the investigated tree species diversity gradient. However, the differences in stand characteristics are probably not typical for other forests, which might for example have larger canopy roughness in mixed compared to single species stands.

The ions Cl^-, SO_4^{2-}, H^+, NH_4^+ and NO_3^- may also be deposited as gases (ID_{gas}). Because it was not possible to estimate ID_{gas}, the total deposition and the canopy uptake of these ions might be underestimated and the canopy leaching overestimated. For example, the canopy uptake of NH_4^+ is likely to be underestimated, whereas the canopy leaching of NO_3^- overestimated. Since the gaseous deposition is influenced by the stand characteristics, the actual differences in canopy exchange between the diversity levels might differ somewhat from the calculated differences. Hence, the interception and total deposition of these ions and also the calculated canopy exchange have to be interpreted with care.

Canopy exchange of ions can be due to passive diffusion between the water layer covering the leaves and the apoplast or due to ion exchange by cuticular exchange sites (Draaijers et al. 1994). Several factors affect these processes, some of which probably do not differ among the studied forest plots (foliar wax degradation, amount and duration of precipitation and abiotic stresses), whereas others do. These are the wettability of foliage, which is found to differ considerably among tree species, tree physiology and age distribution of leaves (Draaijers et al. 1994). Hence, differences in the canopy exchange between the diversity levels may be due to differences in the above mentioned factors among the tree species. In addition, the differences in canopy exchange may also be owing to differences in soil properties, which are likely to have an impact on the foliar ion status and would affect canopy exchange (Nordén 1991).

Similar to the stand deposition, the canopy exchange rates of the investigated forest plots differed between the diversity levels (exceptions being Al^{3+}, NH_4^+ and NO_3^-), and for the ions Cl^-, K^+, Ca^{2+}, H^+ and Mn^{2+} CE rates were also related to the Shannon index. Most of the investigated ions were leached from the canopies; only NH_4^+ and in mixed species plots also

H^+ were taken up by the canopy. Na^+ was assumed to be neither leached from nor taken up by the trees. The leaching of Cl^-, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-} and SO_4^{2-} increased, whereas the leaching of the soil acidifying ions Mn^{2+} and H^+ decreased with increasing diversity level. The pronounced leaching of Mn^{2+} in the pure beech plots is an indication that the soil properties of the plots were not the same. Mn^{2+} is known to be more mobile and easily plant available under acid soil conditions (Tyler 1976). If the concentration of soluble Mn^{2+} increases in the soil water, the tree roots probably take up more Mn^{2+}, leading to higher leaf contents and canopy leaching rates. The soils of pure beech plots were indeed more acidic than those of the mixed species plots (Guckland et al. 2009) and the amount of Mn^{2+} in both the soil (Guckland et al. 2009) and the soil solution (unpublished data) was highest in pure beech plots.

The different soil properties may also explain the differences in leaching of K^+, Ca^{2+} and Mg^{2+}. The soils of pure beech plots have lower effective cation exchange capacity and base saturation than those of mixed species plots (see Table 1) (Guckland et al. 2009). Hence, the trees can take up more K^+, Ca^{2+} and Mg^{2+} in mixed species plots than in pure beech plots and this in turn leads to higher leaf contents of these ions (Jacob 2009) and to higher leaching rates (Nordén 1991). Similarly, also the higher leaching rates of PO_4^{3-} in the mixed species compared with the pure beech plots may be explained by the different soil properties. Indeed, the mixed species plots have larger phosphorus pools, which are owing to their higher clay contents (Talkner et al. 2009). The canopy leaching of PO_4^{3-} made up 25% (DL1) to 67% (DL3) of the stand deposition. Due to negligible amounts of phosphorus in ambient air and precipitation, canopy leaching can contribute up to 90% of PO_4^{3-} in stand deposition (Parker 1983).

Differences in soil properties probably influenced the former management practices, leading to pure beech stands in areas with low BS, CEC_e and pH. This in turn led to a further decrease in pH and possibly also BS and CEC_e in the pure beech stands due to the soil acidifying properties of beech (Nordén 1994; Finzi et al. 1998; Neirynck et al. 2000) and the lower decay rates of beech litter compared to ash and lime litter (Melillo et al. 1982). The results of Guckland et al. (2009) suggest that species-related differences in the intensity of the cation cycling between soil and tree contributed to the observed differences in soil acidification and BS between the studied forest plots. Hence, the tree species may have contributed to the differences in soil properties.

Furthermore, differences in the physiology and ion status among the tree species may account for the observed differences in canopy exchange rates. Krauß and Heinsdorf (2005) showed that tree species differ in their leaf ion concentrations, independently of the soil properties.

The investigated beech trees tended to have lower concentrations of K^+, Ca^{2+}, Mg^{2+} and PO_4^{3-}-P in green leaves compared to the other deciduous tree species studied (Jacob 2009). This may have contributed to the lower canopy leaching rates of these ions in the pure beech plots. It is important to mention that the concentrations of Ca^{2+}, Mg^{2+} and N_t in green leaves of the investigated beech trees did not differ between the diversity levels, and that the concentration of K^+ was lowest in DL2 plots and that of PO_4^{3-}-P highest in pure beech plots (Jacob 2009). Hence, the differences in soil properties are not reflected by the ion concentrations in green leaves of beech. This is a confirmation of the species-specific differences in ion concentrations found by Krauß and Heinsdorf (2005) and emphasizes that the soil properties do not solely influence the ion status of trees. In addition, in a common garden test with 14 tree species including *T. cordata*, *A. pseudoplatanus*, *A. platanoides*, *F. sylvatica* and *C. betulus*, tree species influenced soil properties directly through variation in the quantity and chemistry of their litter and indirectly through the effect of their litter on detritivores (Reich et al. 2005). These effects led to rapid (within three decades) and widespread changes of soil properties beneath the different tree species (Reich et al. 2005).

The calculated acid input to the canopy was highest in pure beech plots, whereas the acid buffering capacity of the canopy did not differ between the diversity levels. Hence, the higher base saturation of the soils and the additional tree species in the mixed species plots did not lead to a higher canopy buffering capacity compared to the pure beech plots. It is important to keep in mind that H^+ buffering in the canopy removes acidity from stand precipitation, but does not decrease the total H^+ input to the soil. This is because buffering in the canopy occurs by cation exchange from inner leaf tissue surfaces and these cation exchange buffer sites are recharged by cations taken up by the roots through exchange with protons in the rhizosphere of the soil (Ulrich 1983b).

To summarize, we can state that the ion leaching of the cations K^+, Ca^{2+}, Mg^{2+} and the anions Cl^-, PO_4^{3-} and SO_4^{2-} increased along the investigated tree species diversity gradient from monospecific beech plots to tree species rich plots. The leaching of these ions did not only differ between pure beech and mixed species plots but also between the mixed species plots (DL2 and DL3). In contrast, the canopy leaching of the soil acidifying ions Mn^{2+} and H^+ decreased along the investigated tree species diversity gradient from monospecific beech plots to tree species rich plots (with H^+ being taken up in mixed species plots). Here, the difference was most pronounced between pure beech plots and mixed species plots, while mixed species plots did not differ. Regarding the soil properties, significant differences were found between pure beech and mixed species plots, while the mixed species plots (DL2 and DL3) had similar

soil properties. Thus, the canopy exchange of Mn^{2+} and H^{+} may mainly have been influenced by the differences in soil properties, whereas the leaching of K^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, PO_4^{3-} and SO_4^{2-} may also have been influenced by the physiology and ion status of the tree species present in the investigated forest plots.

Conclusion

The results of this observational study showed that atmospheric deposition was influenced by the stand composition (i.e., Shannon index). However, it was not possible to isolate the role of single stand characteristics such as stand height and canopy roughness, since they were correlated. One can assume that this is the case in most natural forest ecosystems. Canopy exchange processes were influenced by differences in ion status between the tree species as well as soil properties. Soil properties that influence canopy exchange processes are pH, cation exchange capacity and base saturation. Trees are known to have an influence on these properties and especially beech trees have been shown to lower pH, base saturation and cation exchange capacity. Hence, in addition to their direct influence on deposition and canopy exchange processes, the tree species also have an indirect effect in the way that they alter the mentioned soil properties, which in turn affect the uptake of ions by the trees and the subsequent canopy exchange.

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Concluding discussion

The hypotheses that were posed in the introduction section are evaluated according to the results of the three papers presented in the main part of the dissertation:

(1) increasing tree species diversity increases the soil phosphorus pools and concentrations and accelerates the annual phosphorus turnover of the leaf, herb layer and fine root litter (Paper 1);

(2) phosphate sorption and transport in forest soils differs from that in agricultural soils and is dependent on soil properties (Paper 2);

(3) increasing tree species diversity increases the phosphorus and nutrient input to the soil due to changes in deposition and canopy exchange processes (Paper 3).

Soil phosphorus pools, concentrations and turnover (Paper 1)

Tree species diversity was not directly responsible for differences in soil phosphorus pools and concentrations. The differences in soil phosphorus between the diversity levels were mainly explained by the differences in clay content of the studied forest soils. In general, the pure beech stands were found on more acidic soils with lower clay contents, base saturation and cation exchange capacity. This finding illustrates the general problem of observational studies that covarying factors (like the clay content) make it difficult to determine causality (Scherer-Lorenzen *et al*., 2005; Vilà *et al*., 2005).

However, the phosphorus input with the leaf litter tended to increase with increasing tree species diversity. In addition, the annual turnover of phosphorus with leaf litter, herb layer litter and fine roots was influenced by the tree species composition. The phosphorus transport from litter into soil was much faster in the mixed species stands than in pure beech stands. These differences in turnover time are mainly ascribed to differences in litter quality of the tree species and to differences in bioturbation due to differing communities of the soil biota. The latter again are influenced by the soil properties, namely the pH values.

Furthermore, we found low soil phosphorus and leaf litter concentrations compared to other studies (e.g., Rubaek *et al.*, 1999; Krauß & Heinsdorf, 2005), indicating that the studied forest stands had an insufficient phosphorus supply.

In conclusion, the hypothesis that increasing tree species diversity accelerates the annual phosphorus turnover of the leaf, herb layer and fine root litter was confirmed. However, the higher soil phosphorus pools and concentrations of the mixed species stands could mainly be

explained by their higher soil clay contents and tree species did at least not have a direct effect on soil phosphorus pools and concentrations.

Phosphate sorption and transport (Paper 2)

Phosphate sorption of six of the forest soil samples investigated in the first paper was determined in the laboratory. These soil samples had different pH values, clay contents and organic matter contents and represented the small-scale heterogeneity in soil properties of the study area. The phosphate sorption behavior of the soil samples differed. There was a tendency that the more acid soil samples with low clay contents were best fitted by a linear equation and the soil samples with higher pH values and larger clay contents by the Freundlich equation. Hence, the small-scale heterogeneity of soil properties in the study area seemed to influence the sorption behavior of the soil samples. All soil samples sorbed large amounts of the added phosphate already after one day. This can be seen as the fast sorption process (McGechan & Lewis, 2002; Barrow, 2008) and was assumed to be due to generally low pH and high organic matter contents of forest soils. The desorption of the previously sorbed phosphate was incomplete; hence, only small amounts could be desorbed again. This finding explains the fact that the phosphate concentration in forest soil solutions is very low (in the studied soils: 0.02-0.08 mg L^{-1}). The longer the contact time of phosphate with the forest soil, the stronger is the binding and it may be assumed that this leads to decreased plant availability of phosphorus (Barekzai, 1984). Hence, the plants either have to take up phosphate very fast from the soil solution before it is sorbed by the soil or they have to use mechanisms that assist desorption of phosphate. These mechanisms can be root-induced chemical processes (e.g., the release of exsudates; Hinsinger, 2001) or the symbiosis with mycorrhiza (Schachtman *et al.*, 1998).

In addition, a model describing phosphate transport in soils based on the convection-dispersion equation with a linear adsorption equation (Toride *et al.*, 1999) was applied to data of the investigated forest soil samples. This model did not completely describe the transport of phosphate in the studied soil samples, indicating that other processes like precipitation and dissolution or complexation, which were not considered in the model, influenced the phosphate storage and transport.

In conclusion, the hypothesis that phosphate sorption and transport in forest soils differs from that in agricultural soils and is dependent on soil properties was partly confirmed by the results of the second paper.

Deposition and canopy exchange processes (Paper 3)

The increase in tree species diversity in the investigated forest stands led to changes in the stand structural characteristics. Pure beech stands were taller and the roughness of the canopies was higher than in the mixed species stands. These stand differences lead to different capacities of the canopies to capture airborne ions (Erisman & Draaijers, 2003). Hence, the pure beech stands showed highest interception deposition for both nutrients (K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}) and soil acidifying compounds (Mn^{2+}, H^+). The leaf area played no role in this process in the investigated stands.

The canopy exchange processes also differed between the forest stands. The nutrients K^+, Ca^{2+}, Mg^{2+} and PO_4^{3-} were leached in higher amounts from the mixed species canopies compared to the pure beech canopies, whereas Mn^{2+} and H^+ canopy leaching was highest in pure beech stands. Krauß & Heinsdorf (2005) showed that tree species differ in their leaf ion concentrations. Therefore, the lower canopy leaching rates of K^+, Ca^{2+}, Mg^{2+} and PO_4^{3-} in the pure beech stands may be due to lower concentrations of these ions in beech leaves compared to the other tree species studied. The stand deposition of Al^{3+}, Fe^{2+}, SO_4^{2-}, PO_4^{3-} and N-compounds did not differ substantially between the diversity levels, indicating that tree species composition did not influence the deposition and canopy exchange of these ions.

The high leaching of Mn^{2+} from canopies of pure beech stands pointed to the existing differences in soil properties already discussed in the first and second paper about soil phosphorus. The pure beech stands are more acid and have less exchangeable cations than the mixed species stands (Guckland *et al.*, 2009). This leads to a high mobility of Mn^{2+} and a low availability of base cations in the pure beech soils (Tyler, 1976). Hence, the high Mn^{2+} leaching rates and the comparably low K^+, Ca^{2+} and Mg^{2+} leaching rates of the pure beech canopies may be influenced by the differences in soil properties.

In conclusion, the hypothesis that increasing tree species diversity increases the phosphorus and nutrient input to the soil due to changes in deposition and canopy exchange processes was confirmed for phosphorus, potassium, calcium and magnesium, whereas the acid input to the forest soils was highest in pure beech stands.

Overall conclusion

Increasing tree species diversity accelerated the phosphorus turnover in the studied forests and increased the annual soil input of nutrients due to canopy exchange processes. The most pronounced differences were found between the pure beech stands (DL1) and the mixed

species stands (DL2 and DL3). The differences between the mixed species stands dominated by three tree species (DL2) and those dominated by five tree species (DL3) mostly were minor. The differences in soil properties between the soils of the pure beech and the mixed species stands (e.g., clay content, pH, cation exchange capacity, base saturation) influenced the soil phosphorus pools and concentrations as well as the canopy exchange processes.

It is assumable that former forest use enhanced the growth of valuable deciduous tree species like ash, maple, lime and hornbeam on all the sites where it was possible. Therefore, the sites where pure beech stands are presently found probably have had soil properties not suitable for the growth of the other deciduous tree species, indicating that the differences in soil properties are site specific. Indeed, some of the soil properties that differ between the stands are definitely not affected by trees, e.g., the clay content. However, soil properties that underlie rapid changes can be influenced by the trees and their leaf litter; these are for example pH, cation exchange capacity and base saturation. Especially beech is known for its effect on the pH. Therefore, the growth of different tree species made the existing differences in these soil properties among the forest stands even more extreme.

Hence, the observed differences in the phosphorus pools, concentrations and turnover as well as in the ion deposition and canopy exchange processes between the pure beech and the mixed species stands were due to differences in soil properties and tree species composition. Tree species play besides their direct role also an indirect role in nutrient storage and cycling in the way that they have an effect on soil properties, which in turn lead to changes in the soil phosphorus storage and transport, in the turnover of organic material and in the canopy leaching of ions.

Summary

Soil nutrient pools, concentrations and turnover as well as soil nutrient inputs due to deposition and canopy exchange have been studied intensively in all kinds of forest ecosystems worldwide. In studies about temperate forests, the main focus concerning the macronutrients was on carbon and nitrogen, whereas phosphorus was rather of interest in tropical forests. However, due to increasing nitrogen deposition, phosphorus became or will become a growth limiting factor of many temperate forests. In addition, the changing climate will affect these ecosystems and their nutrient cycling. To be prepared for these changes the establishment of mixed species forests is recommended since mixed forests are supposed to be more resistant and resilient against disturbances than monocultures. In large parts of Central Europe the potential natural forest vegetation is dominated by beech (*Fagus sylvatica* L.). Hence, mixed beech forests are assumed to have a high ecological and economic value in the face of climate change. However, not much is known about the effects of increased tree species diversity on soil nutrients and nutrient cycling in temperate beech forests. Studies about the influence of tree species composition on soil phosphorus pools, concentrations and turnover are almost lacking.

The dissertation on hand compared the soil phosphorus pools, concentrations and turnover of pure beech stands with those of mixed species stands, investigated the phosphate sorption capacity and transport in forest soils and compared the deposition and canopy exchange of phosphorus and other nutrients of pure beech stands with those of mixed species stands. The study area was situated in the largest coherent broad-leaved forest in Germany and could be divided into three different stand types concerning tree species diversity: (1) beech as the main tree species; (2) beech, lime and ash as the main tree species and (3) beech, lime, ash, maple and hornbeam as the main tree species.

The pools and concentrations of both inorganic and especially organically bound phosphorus were smaller in the soils of pure beech stands than in those of mixed species stands. However, these differences mainly could be ascribed to lower clay contents in the pure beech stands, whereas the tree species played a minor role in the storage of phosphorus in these soils. The input of phosphorus to the soil with leaf litter showed a clear tendency to increase with increasing tree species diversity. The turnover time of phosphorus in the organic surface layer was shorter in mixed species stands than in pure beech stands. Hence, the input and turnover was influenced by the tree species. Yet, the lower pH, base saturation and cation exchange

capacity of the pure beech stands influenced the decomposition of leaf litter by changes in the composition of the soil biota.

The soil samples could be separated into two groups according to their phosphate sorption behavior: there was a tendency that the more acid samples with low clay contents were best fitted by a linear equation and the samples with higher pH values and larger clay contents by the Freundlich equation. Hence, the small-scale heterogeneity of soil properties in the study area seemed to influence the sorption behavior of the soil samples. Desorption of previously added phosphate was incomplete. The application of a transport model on our data showed that phosphate transport could not be described well with this kind of adsorption/desorption model. This was probably due to other processes involved in phosphate storage and transport, like precipitation and dissolution, which were not considered in the model.

The deposition of airborne nutrients and acidifying compounds was highest in pure beech stands since they were higher and had rougher canopies compared with the mixed species stands. The canopy leaching of phosphate, potassium, calcium and magnesium was highest in mixed species stands, whereas protons and manganese were mainly leached from pure beech canopies. The differences in ion status and physiology between the tree species may explain the observed differences in canopy exchange. Still, the soil properties also affected the canopy exchange processes. The lower pH of pure beech stands leads to a high mobility of soil manganese and consequently to enhanced manganese uptake by the trees. In addition, the lower base saturation leads to reduced uptake of potassium, calcium and magnesium in the pure beech stands. The beech trees had higher manganese and lower potassium, calcium and magnesium leaf contents than the other tree species, due to both species-specific differences in ion status and differences in soil properties, leading to the described canopy leaching rates.

The results of the dissertation on hand show that it is difficult to clearly separate the effects of tree species diversity from those of soil properties on soil phosphorus and nutrient cycling. The soils of the forest stands originally differed in some of the soil properties, namely the clay content. However, trees are known to alter soil properties which underlie rapid changes, i.e., pH, base saturation and cation exchange capacity. Hence, the soil differences between the pure beech and the mixed species stands became even more pronounced. In conclusion, tree species played a direct as well as an indirect role in nutrient storage and cycling in the way that they had an effect on soil properties, which in turn led to changes in the soil phosphorus storage and transport, in the turnover of organic material and in the canopy leaching of ions.

Zusammenfassung

Nährstoffvorräte, -konzentrationen und -umsätze im Boden sowie Nährstoffeinträge durch Deposition und Kronenraumaustausch wurden weltweit in den verschiedensten Waldökosystemen intensiv untersucht. In Studien über Wälder der gemäßigten Zonen lag der Schwerpunkt hinsichtlich der Makronährstoffe auf Kohlenstoff und Stickstoff, während Phosphor (P) eher in tropischen Wäldern von Interesse war. Im Zuge zunehmender Stickstoffdeposition ist bzw. könnte P jedoch ein wachstumslimitierender Faktor vieler Wälder der gemäßigten Zonen werde. Außerdem wird der Klimawandel diese Ökosysteme und ihre Nährstoffumsätze beeinflussen. Um auf diese Veränderungen vorbereitet zu sein, wird die Einrichtung von Mischwäldern empfohlen, da diese störungsresistenter und belastbarer seien als Monokulturen. In großen Teilen Mitteleuropas wird die potentielle natürliche Vegetation von der Buche (*Fagus sylvatica* L.) dominiert. Deshalb wird vermutet, dass Buchenmischwälder im Hinblick auf den Klimawandel einen hohen ökologischen und ökonomischen Wert haben. Über die Auswirkungen zunehmender Baumartendiversität auf Bodennährstoffe und Nährstoffkreisläufe in gemäßigten Buchenwäldern ist jedoch wenig bekannt. Untersuchungen zum Einfluss der Baumartenzusammensetzung auf P-Vorräte und -konzentrationen im Boden und den P-Umsatz fehlen fast ganz.

Die vorliegende Doktorarbeit verglich die P-Vorräte und -konzentrationen im Boden und den P-Umsatz reiner Buchenbestände mit denen von Mischbeständen, untersuchte die Phosphatsorptionskapazität und den -transport in Waldböden und verglich die Deposition und den Kronenraumaustausch von P und anderen Nährstoffen reiner Buchenbestände mit denen von Mischbeständen. Das Untersuchungsgebiet lag im Nationalpark Hainich, der Teil des größten zusammenhängenden Laubwaldgebiets Deutschlands ist. Es konnte in drei verschiedene Bestandestypen bezüglich der Baumartendiversität eingeteilt werden: (1) Buche als Hauptbaumart; (2) Buche, Linde und Esche als Hauptbaumarten; (3) Buche, Linde, Esche, Ahorn und Hainbuche als Hauptbaumarten.

Die Vorräte und Konzentrationen sowohl von anorganischem als auch besonders von organisch gebundenem P waren geringer in den Böden reiner Buchenbeständen als in denen der Mischbestände. Diese Unterschiede konnten jedoch hauptsächlich den niedrigeren Tongehalten der reinen Buchenbestände zugeschrieben werden, wohingegen die Baumarten eine geringere Rolle in der P-Speicherung dieser Böden spielten. Der P-Eintrag mit der Blattstreu in den Boden zeigte eine klare Tendenz, mit steigender Baumartendiversität

zuzunehmen. Die Umsatzzeit von P in der organischen Auflage war kürzer in Mischbeständen als in reinen Buchenbeständen. Folglich wurde der Eintrag und Umsatz von den Baumarten beeinflusst. Jedoch wurde die Zusammensetzung der Bodenbiota und damit die Streuzersetzung sicherlich auch durch den niedrigeren pH-Wert, die geringere Basensättigung (BS) und Kationenaustauschkapazität (KAK) der reinen Buchenbestände beeinflusst.

Die Bodenproben konnten an Hand ihres Phosphatsorptionsverhaltens in zwei Gruppen eingeteilt werden: für die Proben mit niedrigem pH und geringem Tongehalt war tendenziell eine lineare Anpassung am besten, wohingegen für die Proben mit höheren pH-Werten und größeren Tongehalten eine Anpassung an die Freundlich Gleichung besser war. Folglich scheint die kleinräumige Heterogenität der Bodeneigenschaften im Untersuchungsgebiet, das Sorptionsverhalten der Bodenproben beeinflusst zu haben. Die Desorption des zugegebenen Phosphats war unvollständig. Die Anwendung eines Transportmodells auf unsere Daten zeigte, dass der Phosphattransport in den untersuchten Waldböden mit dieser Art von Adsorptions-/Desorptionsmodell nicht gut beschrieben werden konnte. Dies lag wahrscheinlich an weiteren Prozessen wie Fällung und Lösung, die in diesem Modell nicht berücksichtigt wurden.

Die Deposition von Nährstoffen und von versauernd wirkenden Verbindungen aus der Luft war in den reinen Buchenbeständen am höchsten, da diese verglichen mit den Mischbeständen höher waren und rauere Kronen hatten. Die Kronenraumauswaschung von Phosphat, Kalium, Kalzium und Magnesium war in den Mischbeständen am höchsten, wohingegen Protonen und Mangan hauptsächlich aus den reinen Buchenkronen ausgewaschen wurden. Die Unterschiede der Baumarten im Ionenstatus und in der Physiologie könnten die beobachteten Unterschiede im Kronenraumaustausch erklären. Dennoch beeinflussten auch die Bodeneigenschaften die Kronenraumaustauschprozesse. Der geringe pH-Wert der reinen Buchenbestände führt zu hoher Manganmobilität im Boden und folglich zu erhöhter Manganaufnahme durch die Bäume. Außerdem führt die geringe BS zu verringerter Aufnahme von Kalium, Kalzium und Magnesium in den reinen Buchenbeständen. Durch die baumartenspezifischen Unterschiede im Ionenstatus sowie die unterschiedlichen Bodeneigenschaften hatten die Buchen höhere Mangan- und geringere Kalium-, Kalzium- und Magnesiumgehalte in ihren Blättern als die anderen Baumarten, was zu den beschriebenen Auswaschungsraten führte.

Die Ergebnisse der vorliegenden Doktorarbeit zeigen, dass es schwer ist, die Effekte der Baumartendiversität auf Boden-P und Nährstoffkreisläufe von denen der Bodeneigenschaften klar zu trennen. Die Böden der Waldbestände unterschieden sich ursprünglich in einigen Bodeneigenschaften, v.a. im Tongehalt. Jedoch ist bekannt, dass Bäume Bodeneigenschaften beeinflussen können, die schnellen Veränderungen unterliegen (pH-Wert, BS und KAK). Folglich wurden die Unterschiede zwischen den reinen Buchenbeständen und den Mischbeständen im Laufe der Zeit noch ausgeprägter. Zusammenfassend lässt sich sagen, dass die Baumarten sowohl eine direkte als auch eine indirekte Rolle in der Nährstoffspeicherung und den -kreisläufen der untersuchten Waldbestände spielten. Sie hatten einen Einfluss auf Bodeneigenschaften, die wiederum zu Veränderungen in der P-Speicherung und dem -transport, dem Umsatz von organischem Material und der Kronenraumauswaschung von Ionen führten.

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Appendix

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Ausbildung

	Doktorarbeit (Note: Magna cum laude)
04/2005 – 03/2009	“Dynamics of phosphorus in soils and of nutrients in canopies of deciduous beech forests differing in tree species diversity”; Betreut von Prof. Dr. F. Beese, Abteilung für Ökopedologie der gemäßigten Zonen, Georg-August-Universität Göttingen; Finanziert von der Deutschen Forschungsgemeinschaft (DFG)
	Diplom in Biologie (Note: 1,6)
10/1998 – 09/2004	Ruprecht-Karls-Universität Heidelberg; Fächer: Botanik, Biophysik, Zellbiologie; Diplomarbeit: “Effects of thallium and cadmium on *Brassica juncea* and *Brassica napus*”
	Erasmus-Austausch
08/2001 – 06/2002	Universität Lund, Schweden; Fächer: Ökologie, Bodenkunde, Zellbiologie
	Abitur (Note: 1,5)
08/1989 – 06/1998	Hochrhein Gymnasium Waldshut

Kurse und Praktika

	Externe Doktorandenkurse
08/2007	"Landscape planning and sustainable use of nature resources in a changing world" in Sibirien und dem Altaigebirge; Stipendium vom Deutschen Akademischen Austauschdienst (DAAD)
09/2006	"Biodiversity and Ecosystem Services: Ecological and Socio-Economic Aspects" in Peyresq, Frankreich; Finanziert vom "EU FP6 Network of Excellence: A Long-Term Biodiversity, Ecosystem and Awareness Research Network (ALTER-Net)"; Auszeichnung: 1. Posterpreis
	Praktika
09/2003 – 10/2003	"Stiftung Natur und Umwelt Rheinland-Pfalz", Mainz; eigenständige Projektarbeit, Presse- und Öffentlichkeitsarbeit
09/2002 – 10/2002	Institut für Chemie und Dynamik der Geosphäre (Abteilung Phytosphäre), Forschungszentrum Jülich; Untersuchung des Austauschs von flüchtigen organischen Verbindungen (VOCs) zwischen Pflanze und Atmosphäre

Persönliche Fähigkeiten

Sprachen	**Muttersprache**: Deutsch
	Fremdsprachen: Englisch: fließend in Wort und Schrift Schwedisch: fließend in Wort und Schrift Französisch: Schulkenntnisse Latein: Schulkenntnisse
EDV-Kenntnisse	**Microsoft Office**: Word, Excel und Power Point: sehr gut Access: gut
	Textverarbeitung: LaTex: gut
	Statistik and Grafiken: R: sehr gut SPSS und Sigma Plot: Grundkenntnisse
	Programmiersprache: C++: Grundkenntnisse
Führerschein	Klasse B

Freizeitinteressen

Natursport	Wandern, Langlauf, Kajakfahren
Kunst	Fotografieren, Zeichnen

Göttingen, 16. März 2010

Ulrike Talkner